Enhancement of Chemical Products in Bio-Crude-Oil from Lignocellulosic Residues – Effects of Biomass Type, Temperature, Pre-treatment and Catalysts.

Dissertation

Zur Erlangung des Doktorgrades

vorgelegt von

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Hamburg 2011

Universität Hamburg
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Genehmigt vom Fachbereich Biologie
der Fakultät für Mathematik, Informatik und Naturwissenschaften
an der Universität Hamburg
auf Antrag von Priv..-Doz. Dr. J. ODERMATT
Weiterer Gutachter der Dissertation:
Prof. Dr. T. BRIDGWATER
Tag der Disputation: 29. Juni 2011

Hamburg, den 14. Juni 2011

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I hereby declare that this research work was carried out by me, Azeez Mayowa Akeem, at the University of Hamburg (Institute of Wood Science) in collaboration with Wood Chemistry/Chemical Technology Unit of Johann-Heinrich von Thünen Institute, Hamburg, between April 2008 and March 2011. And that all experiments and analyses herein reported were carried out at the Wood Chemistry/Chemical Technology Unit of Johann-Heinrich von Thünen Institute, Bergedorf, Hamburg.

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Acknowledgement

My special thanks goes to Dr. Dietrich Meier for supervising this work and his persistent words of encouragement. The unwavering support, trust and useful suggestions from my official supervisor, in person of Dr. Jürgen Odermatt, are greatly appreciated. I am equally grateful to Prof. Ing. Thomas Willner, who is instrumental to my sojourn to Hamburg and at the same time offered to co-supervise this research. The trio have contributed immensely to the successful completion of this program with enriched ideas, thorough supervision coupled with love. Their charming disposition is worthy of emulation. I will ever remain grateful.

My interaction in the course of this work was unrestricted in all units within the Institute, largely due to open arms and affections of all workers. I am grateful to Dr. Jürgen Puls (Institute Acting Director), Prof. Bodo Saake, Dr. Ralf Lehnen and Dr. Othar Kordsachia, for their numerous assistances.

The completion of this research has been attained with assistances rendered by my colleagues and co-workers; Ingrid Fortmann, Silke Radtke, Michael Windt, Eoin Butler, Tina Schirmacher, Gudrum Jesussek, Christiane Riegert, Christiane Kühl and Cornelia Hamann. Supports from other colleagues; Philip Wenig, Andreas Klingberg, Alexander Deutschle, Fokko Schütt and Valentina Becerra are also appreciated. Your love and affection have made my stay in the institute seemingly short. In the same vein, I appreciate help offered by Martina Heitmann, Inge Stichweh, Patrick Eidam, Bernhard Ziegler, Nikole Erasmy, Manuela Mauerhöfer (Secretary), Tanja Potsch and other co-workers. You have all touched my life positively. I am thankful.

The full scholarship offered by Deutscher Akademischer Austausch- Dienst (DAAD) throughout the period of this research work has provided me the enabling condition to carry out this work without hindrance. I am immensely thankful to DAAD for this gesture. My employer, University of Ado-Ekiti, Nigeria is equally appreciated for the trust reposed in me and also for her support and assistance by granting me study leave.

This appreciation will be incomplete without mentioning invaluable contributions by my spouse and my three boys. They have sacrificed their feelings and emotions to enable me attain this height. I thank you for your affection, love and understanding. I remain highly indebted to you. I equally thank my parents, brothers and sisters for their care and prayers. You are such wonderful parents and siblings.

Above all, all Praises and Thanks are due to Almighty God, the Giver of my strength and guidance. And Him alone shall I worship.

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1 Introduction

1.1 Production of fuels and chemicals from biomass

The production of fuels and chemicals from a wide range of renewable resources via various conversion processes is one of the important global issues. Renewable and non-food biomass has the potential to generate inexpensive organic chemicals and fuels if they are efficiently converted via an appropriate processing route. For instance, biomass can be transformed into biogas through fermentation, processed into several chemicals through biochemical processes (hydrolysis and fermentation), pyrolysed to liquid chemicals and fuel, and gasified to produce syngas. Syngas can be used to synthesis chemicals and fuels (BRIENS et al., 2008). To harness beneficial gains of various conversion processes, an all-encompassing approach using multi-conversion processes may be required. This will enable efficient conversion of various components of lignocellulosic biomass to economic end user chemical products. In line with this thought, the concept of biorefinery is under development, whereby lignocellulosic biomass is transformed through intermediate monomeric and polymeric units to obtain bio-fuels and chemicals. This conversion approach is similar to petroleum refinery (BOZELL, 2008; CHERUBINI, 2010; CLARK, 2007; CLARK et al., 2006). The integrated process is expected to give zero waste by-products, using a combination of different biochemical and thermochemical conversion processes (also aided by catalytic modifications). An illustrative concept of possible conversion processes within the system, according to Stoker (2008), is depicted in Figure 1.1.

There are arrays of chemicals, obtainable from lignocellulose biomass. Some of these are derivable in substantial quantities, depending on the method of conversion. From glucose and other constituent repeating units (for example xylose), numerous chemicals such as furfural, 5-hydroxymethyl furfural (HMF), 3-hydroxy propionic acid, 2,5 furan dicarboxylic acid, 5-(Glucosyloxymethyl)furfural (GMF), 3-hydroxybutyrolactone, glycerol and many 1,4-dicarboxylic acids can be produced (LICHTENTHALER, 2002; WERPY and PETERSEN, 2004). Other chemical products from organic raw materials are methanol, ethanol, levoglucosan, acetic acid, hydrogen, carbon monoxide, arabinitol, sorbitol and levulinic acid. Some of these chemicals have been identified and classified among potential top 30 chemical building blocks, which can be processed to obtain more valuable chemical products (WERPY and PETERSEN, 2004). For example, 3-HMF is a potential bio-based chemical feedstock, from which arrays of useful chemicals such as acids, aldehydes, alcohols, amines and 2,5-

dimethylfuran(DMF) can be obtained. DMF, with an energy content of 31.5MJ/L, is a potential fuel in the nearest future (BINDER and RAINES, 2009; ROMAN-LESHKOV et al., 2007).

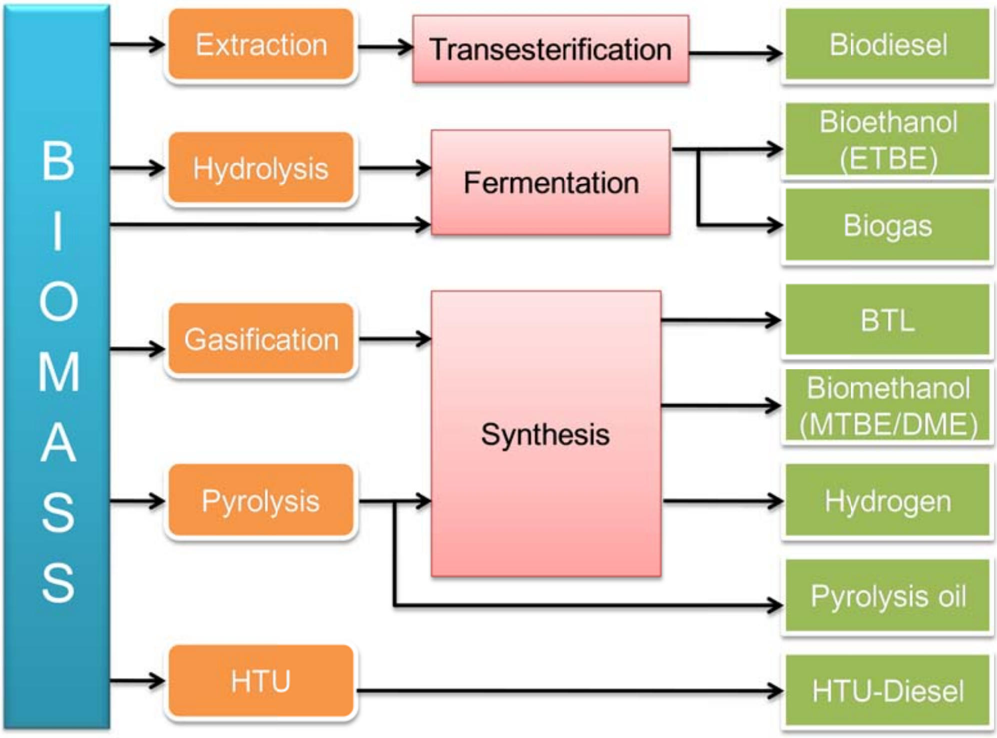


Figure 1.1: Simplified process flow in a lignocellulosic biorefinery (Stocker, 2008)

Also, the complex lignin macromolecule can be converted to obtain phenolic chemical feedstock. Lists of aromatic products derivable from this hetero-polymer are inexhaustible. They include BTX chemicals (benzene, toluene, xylene), phenol, lignin monomer molecules (eugenol, syringols, guaicols), oxidized lignin monomers (syringaldehyde, vanillin) and aromatic polyols (cresols, catechols, resorcinols), just to mention a few. Additionally, these chemicals can be processed to obtain wide varieties of new products (BOZELL, 2008; BOZELL et al., 2007).

The production of hydrogen and carbon monoxide from biomass offers a promising prospect on the production of biobased chemicals. This stems from its ease of convertibility to higher value products; synthetic petroleum (via Fischer-Tropsch process), methanol, dimethylether and ammonia (MASCHIO et al., 1994). But, low purity due to the presence of chemical species, such as oxides of potassium, calcium and silicon, aldehydes and mixed alcohols, challenges the economic viability of the process (DAYTON, 2003; LEIBOLD et al., 2008). However, with adequate and effective gas cleaning processes, this problem can be ameliorated. In this respect, a system known as High Temperature and High Pressure (HTHP) syngas cleaning has been developed to enhance the quality of the syngas to the required standard (LEIBOLD et al., 2008).

Biofuel is a term used in reference to liquid or gaseous fuels obtained from biomass: plants, agricultural crops, forestry residues and municipal wastes (DEMIRBAS, 2009). This term does not however exclude biodiesel derived from both vegetable and animal fats and oils through transesterification. Biofuels can serve as easy substitutes for petroleum based products used in transportation systems, industrial power generation and as raw materials for chemical industries (BRIDGWATER, 1996). Biofuels can be generated from biomass through chemical, biochemical and thermo-chemical processes (KUCUK and DEMIRBAS, 1997). Biodiesel is basically generated through chemical processes. Bioethanol on the other hand can be produced from crops and plants residues through biochemical processes (involving the use of enzymes and microorganisms for fermentation). This conversion process is often preceded by the hydrolysis of feedstock using mineral acid (chemical process).

The production of bio-fuels from lignocellulosic biomass is gaining momentum. This development is due to its advantage of no food-fuel competition, compared to other means of bio-ethanol production, such as the use of cereals. The conversion can be achieved through biochemical (cellulolysis) and thermo-chemical processes (GRAY et al., 2006; WYMAN, 1994). Cellullolysis involves enzymatic hydrolysis of pre-treated lignocellulosic materials to obtain glucose. The resulting product is then fermented and distilled to obtain ethanol. On the order hand, the cellulose can be gasified to hydrogen and carbon monoxide, which are further converted to ethanol through chemical catalysis or fermentation.

1.2 Nigeria and renewable energy

With appropriate governmental policy, researches towards attaining sustainable supply of renewable energy from biomass have reached advanced stages in developed and many developing countries. The biofuels energy policy of the European Union (EU) Commission targets 20% use of biofuel by 2020 (STOCKER, 2008). Efforts are underway to fully harness energy and chemical potentials of lignocellulosic biomass in novel biorefinery concepts. The realisation of vast opportunities in green energy however still largely eludes many African countries, despite their large agricultural resources (DIONCO-ADETAYO, 2001; HALL and SCRASE, 2005).

Abundant lignocellulosic wastes from wood processing and crops residues are annually generated in Africa. For instance, it has been reported that over 58 million tonnes of agricultural residues were generated in Nigeria in 2004 and (higher projection of) 80 million tonnes in 2010 (JEKAYINFA and SCHOLZ, 2009). These unofficial estimates obtained from selected crop residues such as maize, cassava, millet, plantain, groundnut, sorghum, oil palm kernel and cowpeas excludes approximately 2 million tonne/yr sawdust (2000 data) generated from wood processing industries (SAMBO, 2009). In addition, there are several million tonnes of forestry wastes generated, which have not been accurately accounted for.

Due to poor developmental planning, incoherent policies and lack of processing facilities, agro-wastes, like many other waste, are often incinerated or left to rot. Nigeria is the most populous African country. But, it is categorised along countries with the lowest per capita energy consumption. This is due to lack of necessary technological infrastructure to harness energy from her huge hydrocarbon deposit and lack of clear policy on renewable energy options. More than 60% of the population depend on firewood for domestic energy (JEKAYINFA and SCHOLZ, 2009). Meanwhile, availability of energy constitutes an integral part of economic development. JEKANYINFA and SCHOLZ (2009) noted that agro-wastes generated in 2004 alone from selected crops in Nigeria had an estimated energy potential of about 20.8 million tonnes oil equivalent. The production of renewable energy and chemical products from these underutilized agricultural wastes and forestry residues can offer great economic advantage and at the same time, reduce wastes volume.

1.3 Research aims and objectives

Numerous researches and investigations have been carried out on various applications of biomass, towards solving our ever increasing energy needs. The focus of most of these investigations has been, obtaining (liquid and gaseous) products that could serve as easy substitutes to petroleum based fuels. There has been less emphasis on the application of these renewable resources in the production of chemicals. However, exploring this option is also another veritable means of reducing our dependence on petroleum and contributing to cleaner environment, since most of the chemicals in use at present are petroleum derived products. Attainment of this noble goal only requires the establishment of effective conversion strategies through which yields of important chemical products from lignocelluloses can be enhanced. This research focuses on effects of conversion parameters on yields of chemical products in pyrolysates obtained from lignocellulosic residues. It aims at studying various means of increasing yields of valuable chemical products in biomass pyrolysates. Variations to be studied include effects of biomass species, temperature, feedstock pre-treatment and application of catalyst. Underlying differences in the chemical composition of pyrolysates obtained from African biomass residues (sawdust and corncob) and woody wood residue from Europe are to be examined. Effects of feedstock pretreatment on the chemical composition of pyrolysates are to be evaluated using analytical pyrolysis. The influence of various catalysts (such as alkali/alkaline earth metals and zeolites) on organic liquid products (pyrolysate) will also be studied. Prior to the conversion processes, compositional analyses of the raw samples are to be carried out, in order to determine major and minor constituents of the lignocellulosic biomasses. The major part of the research has been published in three peer reviewed articles. These publications, together with some unpublished results, are summarised in chapter three of this manuscript while related basic literature works on biomass and technical pyrolysis are found in chapter two.

2 Literature Review

2.1 Lignocellulosic biomass and its conversion to fuel and chemicals

Lignocellulosic biomass is the generic term used in renewable energy, in reference to wood waste (sawdust and pulp wastes), agricultural residues, energy crops (fast growing grasses) and municipal paper wastes. It is the most abundant and inexpensive energy feedstock. With energy content of approximately 18-19 MJ/kg, lignocellulosic biomass has found applications in the area of renewable energy through different conversion methods to generate liquid fuels and chemicals (AGBLEVOR et al., 1995; KUCUK and DEMIRBAS, 1997; LIN et al., 2010).

2.1.1 Structure and composition of lignocellulosic biomass

In terms of main composition, lignocellulose consists of holocellulose (70-78%) and lignin (22-30%), from which the term lignocellulose is derived. The holocellulose represents the entire polysaccharide constituents that comprise of cellulose (40-50%) and hemicellulose (25-35%). These three principal components form the integral structure of biomass. Beside these main constituents, lignocellulosic biomass contains accessory components in forms of organic (extractives) and inorganic (macro and micro elements). These constituents are formed around dead and living plant cells, arranged and proportioned in different fractions depending on the part and type of plant. The decomposition of these various biopolymers via thermochemical routes subsequently produces various chemical products with related links to the original composition. Thermochemical conversion of lignocellulose is chemically complex because of multitude intrinsic reactions involved. Concise descriptions of biomass constituents are described in subsections below.

2.1.1.1 Cellulose

Cellulose is the main constituent of cell walls of lignocellulosic biomass. With an annual production of 1.5 teratonnes, this inexhaustible biopolymer is considered the most abundant organic matter on earth (KLEMM et al., 2005). It has the molecular formula of $(C_6H_{10}O_5)n$. Cellulose is a homopolymeric saccharide that is made up of (linear chains of) anhydro-β-D-glucose units interlinked through (1→4) glucosidic bonds (SJÖSTRÖM, 1993). The length of cellobiose as the repeating units is said to be 1.03nm (FENGEL and WEGENER, 1984). Cellulose molecules contain 2000-15000 glucosidic monomers positioned at an angle of 180^o through the $^4C_1$ conformation as shown in Figure 2.1, depending on type and part of biomass. The high tensile strength and crystallinity of cellulose, as a polymer, is largely derived from the occurrence of intra- (O3H→O5` and O6→H-O2`) and intermolecular (O6-H→O3`) hydrogen bonds (MOHAN et al., 2006). This super molecular structure is responsible for the insolubility of cellulose in most solvents including water (SJÖSTRÖM, 1993). It is however soluble in alkali, which is capable of breaking the glycosidic bond even at room temperature to yield glucose monomers. Cellulose is hydrolysable with concentrated acids and dissolves in compounds in which it is able to form complexes such as cadmium ethylenediamine complex (ALGER, 1997). The amorphous parts can be hydrolysed using dilute acids.

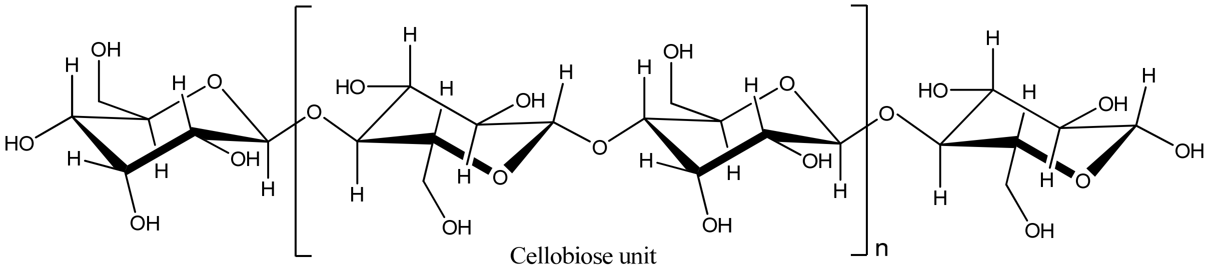


Figure 2.1: Chemical structure of cellulose (MOHAN et al., 2006)

The intermolecular hydrogen bonding stiffens cellulose molecules, facilitating the formation of microfibrils, which consists of about 66 cellulose molecules, ordered in crystallites with disrupted amorphous parts. The microfibrils made up macro fibrils, the so called fabril-aggregates forming the superstructures of cellulose (SJÖSTRÖM, 1993). Owning to high crystallinity with long range order, cellulose requires up to 320^{o}C at 25MPa to undergo amorphous transition (DEGUCHI et al., 2006). The rigidity of the polymer, which varies in different lignocellulose, provides structural support for plants.

2.1.1.2 Hemicelluloses

Hemicelluloses are the second important polysaccharides found in lignocelluloses. They function as supporting materials in cell walls, where their highest concentration is found. They form networks of cross-linked fibres by binding with pectin and cellulose. In contrast to cellulose, hemicelluloses, otherwise known as polyoses, are heterogeneous and highly branched polysaccharides with an average degree of polymerization of about 200 (SJÖSTRÖM, 1993). They are made of pentoses and hexoses, hexuronic acids and deoxy-hexoses anhydrosugars, whose structures are shown in Figure 2.2. Hemicelluloses exist as heteropolymers, except in the case of xylan in some plant species (GÍRIO et al., 2010). The nature and contents of this heteropolymer chain vary, depending on the type of lignocellulosic biomass. For example in softwood, galactoglucomannans are the main hemicelluloses, followed by arabinoglucuronoxylan and arabinogalactan. The hemicelluloses of hardwood mainly consist of glucuronoxylan with small amounts of glucomannan. Apart from these main heteropolymer chains, traces of D-galactosyluronic acid, D-galactose, L-arabinose and L-rhamnose are often found in starch and pectic substance (Sjöström, 1993).

Due to low degree of polymerisation, hemicellulose is less marked in fibre forming property. They are very soluble in hot water, alkali and can easily be hydrolysed to simple sugars using dilute acids. They are chemically less specific compared to cellulose and may give lesser yield of specific chemicals in lignocellulosic biomass conversion to renewable fuels and energy.

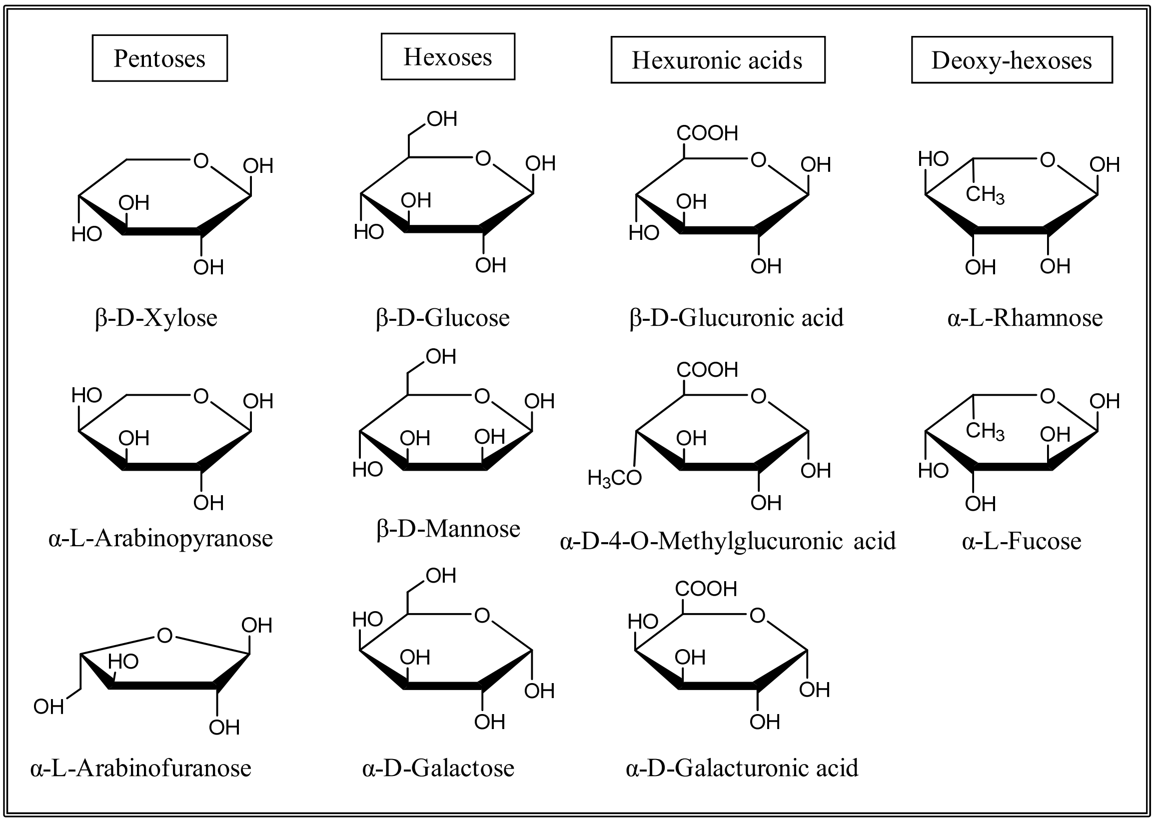
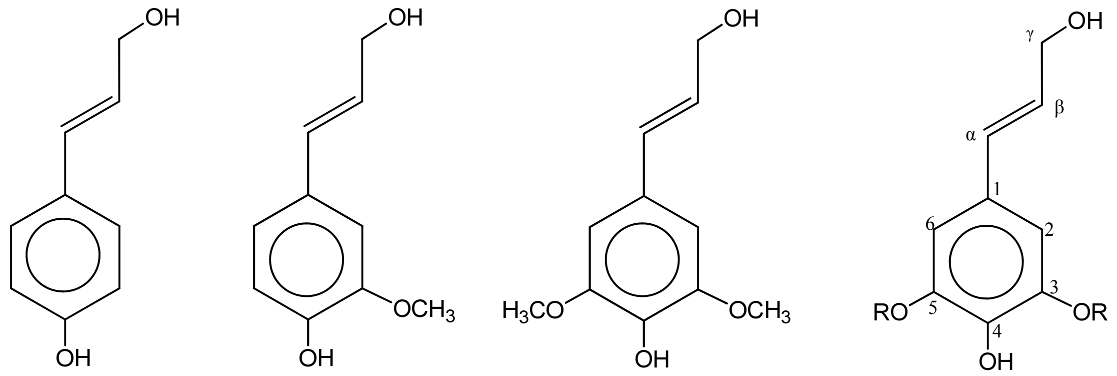


Figure 2.2: Structures of polyoses monosaccharide sugars (Fengel and Wegener, 1984).

2.1.1.3 Lignin

Lignin is a complex amorphous polymeric substance, found in lignocellulose biomass, as an integral constituent of the secondary cell wall, cementing the holocellulose polymer. It largely contributes to the mechanical strength of plants, making it possible for 100m long trees to be able to stand upright (Fengel and Wegener, 1984). It makes up 20-35% of the organic component of wood and ranks next to cellulose, as the second most abundant organic polymer on Earth (Boerjan et al., 2003; Kleinert and Barth, 2008; Sjöström, 1993). Its distribution within different parts of lignocellulosic plants is irregular, with the highest concentration found in the middle lamella cum primary cell wall. It is the most hydrophobic component of biomass main components and is lesser biodegradable than holocellulose. In terms of chemical structure, lignin is a biopolymer consisting of phenylpropanoid units namely; p-hydroxylphenyl (H), guaiacyl (G) and syringyl (S), whereby the phenyl ring is substituted with hydroxyl and alkoxyl groups, depending on the type of wood or plant. The three basic precursors of lignin monomers (known as lignols) are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Boerjan et al., 2003; Fengel and Wegener, 1984). These lignols (depicted in Figure 2.3) are distinguishing features of different types of lignocellulosic biomass. Coniferyl alcohol is the main lignin precursor in all gymnosperms with over 80% of the lignin content. The lignin of angiosperms consists of different compositions of coniferyl and sinapyl alcohols, while that of Gramineae has relatively high amount of coumaryl alcohol (Sjöström, 1993)



p-Coumaryl alcohol

Coniferyl alcohol

Syringyl alcohol

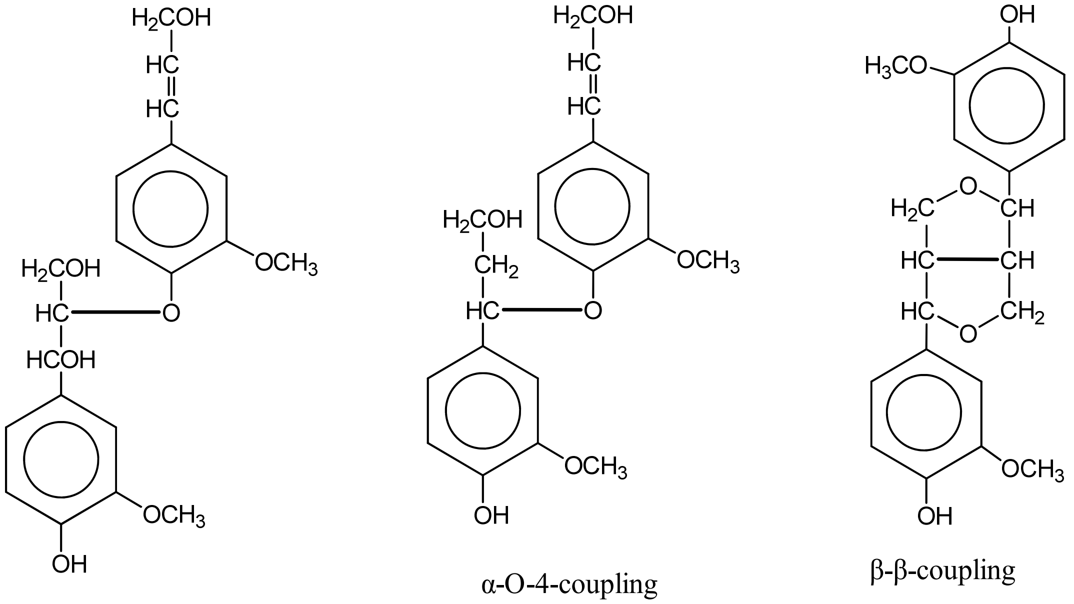
Designations of carbon atoms

Figure 2.3: Monomers of lignin and their carbons' designation.

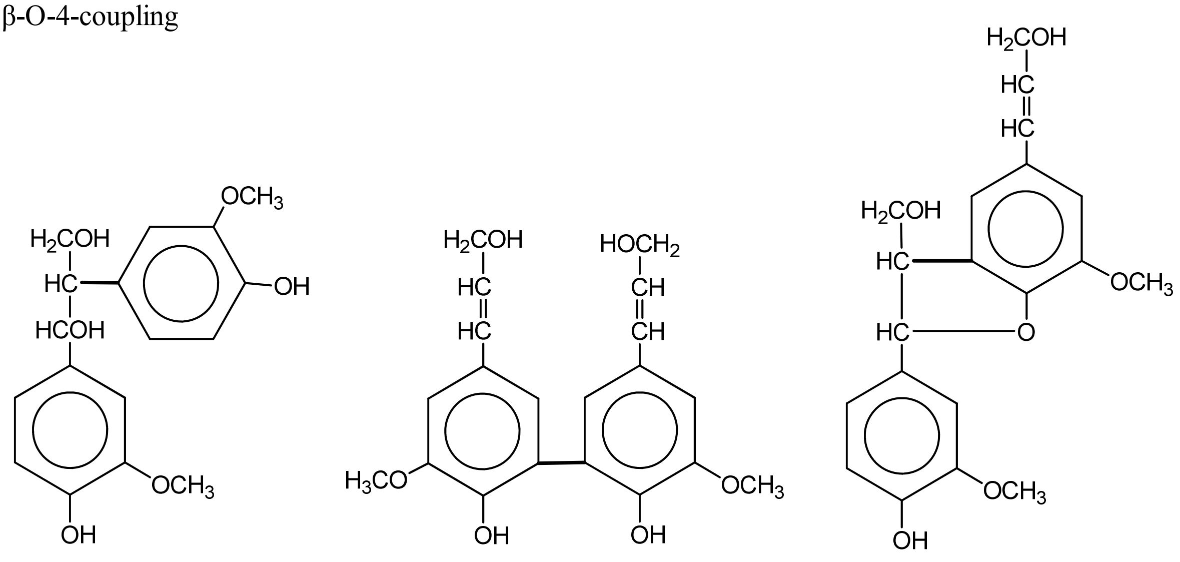
The combination of lignols to form dimer, trimer and other oligomeric lignols through enzymatic-initiated polymerisation reactions give rise to different bonding within lignin macromolecule as shown in Figure 2.4. The frequency of occurrence of these bonding types varies depending on the lignocellulose type. According to Fengel and Wegener (1984), the β-O-4 linkage is the most frequent bonding type in gymnosperms and angiosperms, due to high π-electron densities around methoxy (oxygen atom) group(s) at the *meta*-positions on the phenyl ring. Other authors have noted that this bonding occurrence in softwood is about 50%, followed by 5-5, α-O-4 and β-5 while β-1 and β-β are sparingly found (Pu et al., 2008).

2.1.1.4 Extractives

Extractives are various compounds with low oxygen content such as terpenes, polyphenols, fatty alcohols and fatty acids found mostly in woody biomass. They are lipophilic and hydrophilic compounds. Their functions in wood include colouration, natural durability, protection against insects and fungal attack. They constitute an important raw material for organic chemical production and have a high biological importance (SJÖSTRÖM, 1993). Often found in low amounts, their contents and compositions vary among biomasses, depending on type and part of wood, storage time and location (VARHEGYI et al., 2004). Bark free lignocellulose biomass may contain 4-5 times less extractives than bark containing woods (OASMAA et al., 2003a). This partly explains the higher extractive content in forestry residue compared to other lignocellulose biomass. The rapid reduction in total extractives on storage is largely due to the volatility of terpenes, and hydrolysis of both triglycerides and stearyl esters (OASMAA et al., 2003a).



β-O-4-coupling α-O-4-coupling β-β-coupling



β-1-coupling 5-5-coupling β-5-coupling

Figure 2.4: Typical dilignol structures with common linkages (FENGEL and WEGENER, 1984)

Extractives are located in specific morphological sites within wood structure. The resin acids are found in resin canals, fats and waxes are in the ray parenchyma cells while the phenolic types are present in bark and heartwood (SJÖSTRÖM, 1993). Extractives content in a woody biomass can be extracted using organic solvents but the extraction functions best with the combination of polar and non-polar solvent in sequential steps. However, polar solvents such as methanol and water (especially) may cause slight removal of some hemicellulose and ash contents.

2.1.1.5 Ash

The inorganic component of lignocellulosic biomass constitutes the ash content. The most predominant element in wood ash is calcium, followed by potassium, magnesium and sodium. These elements make up about 82-95% of the total mineral content. The sum of other elements is often less than 1% (FENGEL and WEGENER, 1984). They exist as carbonates, phosphates, silicates and sulphates and located in the wood cell wall (partially bound to carboxyl groups in xylan) and lumina (SJÖSTRÖM, 1993). Similar to extractives, ash content of bark is 10 times higher than amount found in other parts of wood. Ash constituents located in the lumen especially, the alkali and alkaline earth metals are simply removable by washing with water. However, those bound to the cell wall through complexation especially heavy metals are only removable using aqueous acid or complexing agents.

Ash content varies among different lignocellulosic biomasses. And geographic location is another strong influencing factor. Ash content of most temperate woody biomass is often less than 1% whereas in tropical wood types, it could be as high as 5%. Annual plants such as straw and husk can have up to 25% inorganic salt content (FAIX, 2004a; RAVEENDRAN et al., 1995).

2.1.2 Analysis of lignocellulose

Chemical characterisation of lignocellulosic biomass is an essential tool needed in adjudging the usefulness of different feedstocks. With the growing interest in the conversion of biomass to fuel and chemical, the efficiency of conversion processes will be greatly hindered without a proper feedstock analysis. Owing to the complexity of lignocellulose macrostructure, great skill is often required to selectively separate these components from one another for effective chemical analyses. This is because of the intrinsic ultra-structural and chemical combinations among different constituents. In addition, the wood components exhibit different chemical behaviour. They therefore needed to be distinctively analysed.

In actual fact, there is no unified analytical method for the analysis of wood major and minor components (AGBLEVOR et al., 1997). The available methods are collections of those used in scientific researches and industries. Modified methods are often applied, besides the classical analytical methods, to overcome aforementioned compositional complexity (FENGEL and WEGENER, 1984).

As stated above, for proper analyses, separation of different components of lignocellulosic biomass is required. The main task in this regard concerns the use of appropriate isolation and purification methods that meet analyses goals. There are several diverse analytical methods used by various industries (such as the pulp and paper or the forage and food industry). Their utilization of biomass requires detailed feedstock analyses. Amongst the most popular methods are the TAPPI (Technical Association of Pulp and Paper Industry) and ASTM (American Society of Material and Testing) methods used by pulp/paper and wood industries respectively. The National Renewable Energy Laboratory (NREL) has also developed some analytical standards for compositional analysis of renewable feedstock for energy purpose. They mostly involve physical test, measurements and summative analyses of different biomass components.

In concise, analyses of extractive, ash and main components of the cell wall, holocellulose and lignin can be broadly carried out while more detailed analyses will involve the determination of different functional groups in each of the components. The analysis of the main components is carried out using extract-free sample since the extractives can negatively influence subsequent analyses owning to their partial removal.

For the extractives analysis, the simplest method involves the use of soxhlet extraction with different organic extraction solvents ranging from non-polar to polar, to obtain various classes of compounds. The amount of extractives can then be gravimetrically determined following the evaporation of the solvents. The mass of extractives obtained reduces with decrease in solvent polarity; methanol > acetone > dichloromethane > hexane (PENG et al., 2010). No single solvent is capable of removing all the lipophilic extracts, hence combination of solvents work more effective (WALLIS and WEARNE, 1997). However, it has been observed that the relative amounts of lipophilic extracts do not differ in each of the solvent (PENG et al., 2010).

Some common practices involve the combination of polar and non-polar solvents such as toluene–ethanol (2:1, v/v) and chloroform–methanol (2:1, v/v). A successive extraction using petroleum ether, acetone and methanol-water (70/30, v/v) can also be used. Extraction of samples, using Supercritical Fluid Extraction (SFE) and Accelerated Solvent Extraction (ASE) with appropriate solvent, are more modern extraction choices applied nowadays (PENG et al., 2010; WILLFÖR et al., 2005). Detailed analysis of the extract mixtures can be carried out using gas liquid chromatography and high-performance liquid chromatography following appropriate clean-up procedure(s).

The analysis of polysaccharides is carried out following delignification, a step through which the lignin components of the sample are removed. One of the prominent delignification procedures involves the use of acidified sodium chlorite ($NaClO_2$) according to WISE et al. (FAIX, 2004b). The use of chlorine gas, followed by extraction according to the method of VAN BECKUM and RITTER, is another possible route of delignification (FAIX, 2004b). The whitish residue obtained from these reactions is the holocellulose, which can be strategically treated with sodium hydroxide solution for the removal of hemicellulose to obtain different cellulose fractions (FAIX, 2004b).

However, these analytical methods are only appropriate for gravimetric estimations of the holocellulose content. The residue is not entirely lignin free and therefore inappropriate for analysis of constituent sugars. With the availability of modern analytical tools, the determination of the polysaccharides is usually done with total hydrolysis of carbohydrate in biomass, whereby the entire lignin component is obtained as residue. The cell wall polysaccharides are depolymerised into constituent sugars and the solution is quantitatively and qualitatively analysed, using high pressure liquid chromatography (HPLC) or gas chromatography (GC) (DAVIS, 1998; KAAR et al., 1991). For effective depolymerisation of polysaccharides and to minimise the effects of acid resistance by some glycosidic bond, several hydrolysis technique have been developed for effective depolymerisation (DE RUITER et al., 1992; LI et al., 2007; WILLFÖR et al., 2009). In most cases, derivatisation of the polysaccharide is necessary for more accurate analysis.

For gravimetric determination of lignin, the standard method involves digesting the sample with 72% H_2SO_4 in a complete hydrolysis step according to (TAPPI T222 om-88). The residue obtained thereafter is known as Klason's lignin. The acid soluble lignin in the solution can be determined with UV at absorption band of 190nm (SLUITER et al., 2010). A more detailed analysis of lignin will require combination of several analytical techniques and spectroscopy for structural elucidation

The ash analysis is performed using whole sample. The determination is done by oxidising the sample in a furnace at the temperature of 575°C with or without pre-ashing step. The exact inorganic constituents can be analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or Atomic Absorption Spectroscopy (AAS).

2.2 Thermochemical conversion processes of lignocellulose

Thermochemical conversion of biomass involves the use of heat in breaking the complex biopolymer into smaller chemical units, primarily, in a non-reactive environment. It offers efficient and economic means through which gaseous, liquid and solid (char) fuels can be generated from biomass. This process existed and has been utilised much earlier than 18th century, when the first patent right was given to gasification scientist; Robert Gardner (DEMIRBAS, 2010). It has been used to process biomass into charcoal, tar products and gases. The technology development was however abandoned shortly after the discovery of petroleum.

Thermochemical conversion can be categorised into three main routes namely: combustion, gasification, liquefaction and pyrolysis (BALAT, 2008b). This categorisation can be reduced to just pyrolysis and liquefaction, gasification and combustion been forms of pyrolysis with partial and total oxidation of primary products (BRIDGWATER, 2010). Pyrolysis involves the use of elevated temperature in the absence of oxygen to decompose organic matter. The word itself is derived from two Greek elements; *pyr* (fire) and *lysis* (disintegration). Liquid, gas and solid products are obtained from this process but their proportion vary and largely depend on operational parameters, given rise to different forms of pyrolysis modes, a brief detail of which is shown in Table 2.1

Combustion, which is a process of thermal conversion of biomass for the purpose of generating energy and electricity, is here excluded from this categorisation, since the aim is not to generate chemical products, but to abstract the bulk energy content in lignocelluloses. It involves oxidative conversion of organic matters in biomass usually in the presence of excess oxygen (air).

Table 2.1: Modes of pyrolysis and typical yields of their products (dry wood basis)

Mode	*Conditions*	*Liquid*	*Solid*	*Gas*
Fast	~500°C, short hot vapour residence time ~1 s	75%	12% char	13%
Intermediate	~500°C, hot vapour residence time ~10-30 s	50% in 2 phases	25% char	25%
Slow – Torrefaction	~290°C, solid residence time ~30 s	0% if vapour are burned	80% char	20%
Carbonization	~400°C, long vapour residence hour → days	30%	35% char	35%
Gasification	~750-900°C	5%	10% char	85%

(BRIDGWATER, 2010)

Gasification on the other hand is a form of pyrolysis, aims at total decomposition of biomass (at high temperature). Here, gasses such as hydrogen, oxides of carbon and light hydrocarbons are the main products. Fast pyrolysis and liquefaction distinguish themselves from gasification in that both majorly produce liquid products (mixture of several chemical compounds), which can be refined and further processed to obtain valuable chemicals. In addition, gasification can still proceed in environment with limited oxygen; this scenario is undesirable in liquefaction and pyrolysis processes.

Liquefaction involves the depolymerisation of biomass at temperature between 150°C and 420°C and elevated pressure (1-240 bar), using a liquid medium as a heat carrier (BEHRENDT et al., 2008). The use of water as heating and reaction media at temperature of 300-350°C and pressure 12-20 Mpa give raise to the process known as hydrothermal liquefaction. The main difference between this and the most popular thermochemical method (pyrolysis) is the absence of liquid as heating medium in the latter, which is also operated, often at normal pressure.

Pyrolysis has found application not only in the renewable energy but also petroleum industry for breaking heavy petroleum molecules for chemical production (RODRÍGUEZ-REINOSO et al., 2001; TORREGROSA-RODRÍGUEZ et al., 2000). Tobacco industries also rely on this process to examine the burning properties of products (TORIKAIU et al., 2004; WOJTOWICZ et al., 2003).

2.2.1 Fast pyrolysis

Fast pyrolysis refers to pyrolysis process with high heating rates and short reaction times. It involves very fast heating of feedstock (>10K/s) at temperatures of about 500 °C in the absence of oxygen. This results in decomposition of the sample into a mixture of vapours and aerosols. The mixture is rapidly cooled to obtain a condensable organic liquid product (BRIDGWATER and PEACOCKE, 2000; DEMIRBAS and ARIN, 2002). Other by-products are non-condensable gases and char. The principle of fast pyrolysis involves rapid transfer of heat to the particle surface and subsequent transfer of the energy into the particle through conduction. Various biopolymers in the lignocellulose including extractives are defragmented into small condensable vapour and non-condensable gases coupled with char formation. To maximize the condensable liquid product, which is the primary aim of fast pyrolysis, it has been noted that a short residence time of the vapour is required (ACIKGOZ et al., 2004; VENDERBOSCH and PRINS, 2010). Other important parameters include feedstock particle size and chemical composition (ACIKGOZ et al., 2004; LV et al., 2010; SAMOLADA et al., 1990; VARHEGYI et al., 2004).

Fast pyrolysis is applicable to virtually all forms of lignocellulose such as agricultural and forestry wastes to generate liquid products. Several laboratory and semi industrial scale fast pyrolysis units have been employed in investigations with over 100 types of feedstock (BRIDGWATER, 2010). But of greater interest is the liquid product obtained from the process, which offers huge potentials for the derivation of chemicals from renewable sources (BRIDGWATER, 1996).

The reactor, in which the conversion process takes place, is central to the effectiveness of fast pyrolysis. Several types of fast pyrolysis reactors have been developed with the aim of improving the process efficiency, the throughput of the feedstock and the quality of products. With slight variations in composition, the natures of products from these reactors are largely similar. Descriptions of these reactors are well documented in many literature reviews published by different authors (BAHNG et al., 2009; BRIDGWATER, 2010; MEIER and FAIX, 1999; VENDERBOSCH and PRINS, 2010). These reactors include fluidized bed (BOATENG et al., 2007; GARCIA-PEREZ et al., 2008b), circulating fluidized bed (CHEN et al., 2004; DAI et al., 2000), ablative (BECH and JENSEN, 2007; LEDE, 2003), entrained flow type (JARVIS et al., 2010), vortex, auger system (GARCIA-PEREZ et al., 2007; INGRAM et al., 2008) and rotating cone reactor (PARN, 2005).

Of great importance to effective analysis of several pyrolysis volatile products is the online analytical pyrolysis unit coupled to gas chromatography and mass spectrometry (Py/GC-MS). This instrument has been widely applied to study pyrolysed products composition (ALVES et al., 2009; BUDGELL et al., 1987; GALLETTI et al., 1997). It enables better understanding of temperature dependence of volatilisation and pyrolytic dissociation reactions (BOON, 1992). It functions on basic pyrolysis principle like the aforementioned reactors, but in addition, it enables online quantification of the entire volatile products from the reaction, depending on the type of column and detector used.

2.2.1.1 Kinetic and mechanism of fast pyrolysis

Comprehensive knowledge about the mechanisms for the formation of chemical products during the pyrolysis of lignocellulose is an essential tool required in engineering appropriate routes to desired chemical products. However, mastering this knowledge still remains an overwhelming task, especially, in respect to the fast pyrolysis. The major constituents of lignocellulose behave differently during thermal composition. The temperature dependence of these components has been studied using thermo-gravimetric analysis (TGA) by several workers (DE WILD et al., 2009; WILLIAMS and BESLER, 1996; YANG et al., 2007; YANG et al., 2006).

A plot of both TG (in weight %) and differential TG (in % °C^{-1}) against temperature as demonstrated by YANG et al. (2006, 2007) in Figure 2.5 indicates that the first chemical decomposition starts around 220°C and attains maximum at around 260°C for hemicellulose. The DTG plot shows weight-loss rate for this polysaccharide at temperature above 315°C was less than 0.0999 wt.% /°C (YANG et al., 2006). Other authors have however observed that the decomposition ends at around 400°C (VENDERBOSCH and PRINS, 2010). The discrepancy may be due to different heating rates employed in experiments.

Cellulose is slightly more thermally stable than hemicellulose. Its first decomposition occurred around 315°C showing a broad decomposition peak that spans over 90°C (VENDERBOSCH and PRINS, 2010; YANG et al., 2006). This behaviour can be attributed to the presence of high crystalline region in cellulose. The thermal cleavage in cellulose probably commences at the transition point between crystalline to amorphous regions in the polymer chain.

Lignin thermal decomposition is the slowest of all major lignocellulose constituents. It spans the highest temperature range from 160°C up to 900°C (YANG et al., 2006). VENDERBOSCH and PRINS (2010) observed that the conversion of lignin at optimum pyrolysis temperature of 500°C is limited to 40%. They also noted that the solid char residue left after the pyrolysis of biomass (at aforementioned temperature) is mainly derived from lignin.

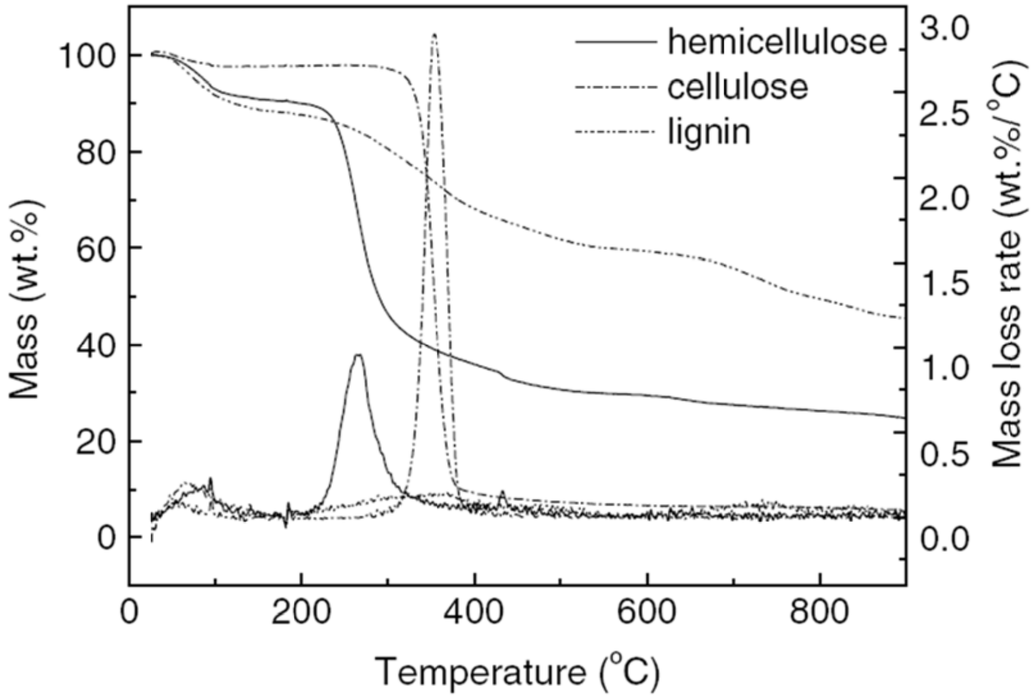
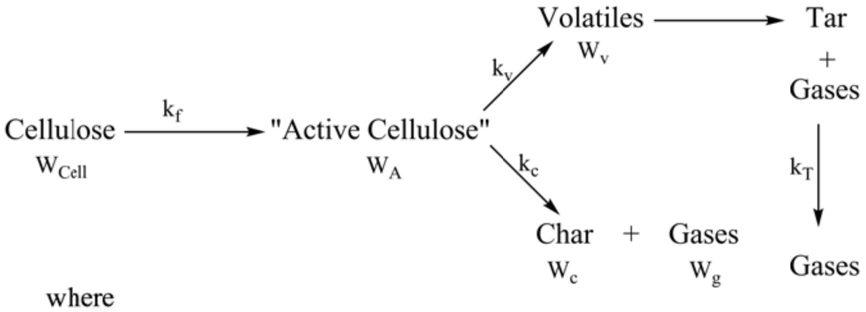


Figure 2.5: Pyrolysis curves of hemicellulose, cellulose and lignin n TGA (Yang et al., 2007; Yang et al., 2006)

Studies on the reaction behaviour of major biopolymer constituents have revealed that the decomposition process is a combination of endothermic and exothermic reactions, with respect to the degradation of lignin and cellulose respectively (PISKORZ et al., 1986). However, it has been noted that the conversion process maintains an exothermic overall energy change (BECIDAN et al., 2007).

Based on early works of Shafizadeh and co-workers, a simple mechanism (model) was proposed that summarises the kinetic event during the pyrolysis of polysaccharides (SHAFIZADEH, 1982; SHAFIZADEH and FU, 1973; SHAFIZADEH et al., 1979). The 'Broido-Shafizadeh model' on the multistep mechanism of cellulose decomposition serves as the basis from which simulation of the reaction kinetic of lignocellulose has been derived by many other authors (PISKORZ et al., 1986; VÁRHEGYI et al., 1997). It describes the formation of active cellulose during heating from which other products emerged according to Figure 2.6.

The validity of this mechanism in fast pyrolysis, under which the formation of volatiles is favoured at the expense of char, however remains a subject of controversy (PISKORZ et al., 1986). Another mechanism known as the random chain cleavage has been proposed (RADLEIN et al., 1991). It represents events in fast pyrolysis with minimum contributions from impurities and alkaline metal adequately (PISKORZ et al., 2000). The zipping model of Shafizadeh however, still serves as good approximation, which is widely employed in explaining pyrolysis mechanism.



where

$$\frac{-d(W_{Cell})}{dt} = k_f(W_{Cell})$$

$$\frac{-d(W_A)}{dt} = k_f(W_{Cell}) - (k_v + k_c)(W_A)$$

$$\frac{-d(W_C)}{dt} = 0.35k_c(W_A)$$

Figure 2.6: Kinetic model for pyrolysis of pure cellulose under vacuum (PISKORZ et al., 1986)

According to DEMIRBAS (2010), the decomposition of lignocellulose during pyrolysis can be simplified into five steps):

- The temperature of the lignocellulose is raised by energy transferred from heating source.
- The primary pyrolysis reaction is initialised at higher temperature leading to the release of volatiles and char.
- Energy is transferred from hot volatiles to cooler regions in the lignocellulose through volatile flow movement.
- Condensation of the volatiles around cooler regions in lignocelluloses is followed by secondary reactions leading to tar production.
- Occurrence of simultaneous and competing reactions between autocatalytic secondary reactions and the primary pyrolytic reactions.

- Depending on the temperature and residence time, occurrence of different processes: continuation of thermal decomposition, reforming, water-gas shift reactions, radicals' combination and possible dehydration.

2.2.1.2 Reaction mechanisms of polysaccharide

The decomposition of polysaccharides has been summarised to involve several competing reaction steps, including depolymerisation via transglycosylation, dehydration, disproportionation, decarboxylation and retro-aldol reactions (BALAT, 2008a; PONDER and RICHARDS, 1993).

On the formation of individual products, SHAFIZADEH et al. (1973) explained the formation of levoglucosan (the main cellulose pyrolysis product) and other anhydrosugars, via the transglycosylation process as shown in Figure 2.7. This conversion occurs following the cleavage of the glycosidic bond.

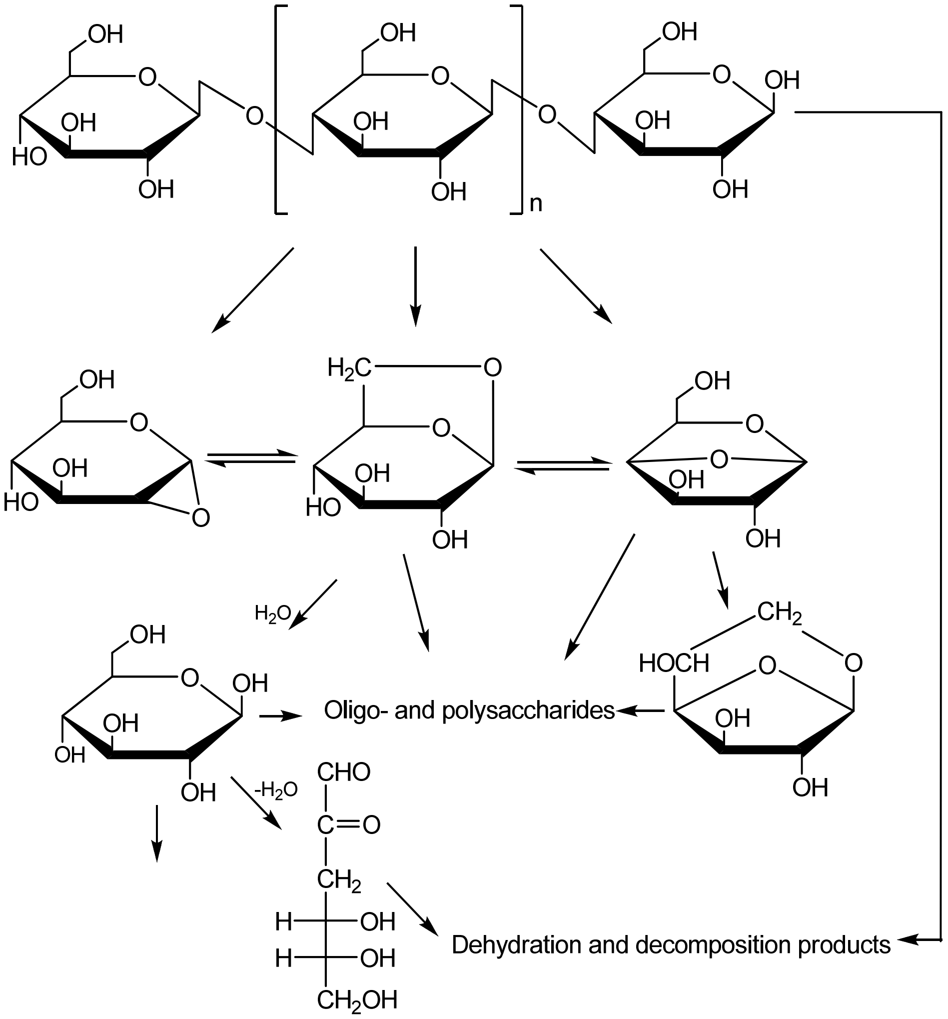


Figure 2.7: Transformation of cellulose products during pyrolysis (SHAFIZADEH and FU, 1973)

They noted that the fate of these anhydrosugars depends on their relative stability and reaction conditions. These probably explain the discrepancy in quantities of anhydrosugars found in the pyrolysate of lignocellulose, as observed by other authors (PISKORZ et al., 1986). Besides levoglucosan, it has been found that dimmeric (cellobiosan) and other polymeric anhydrosugars are also present in the pyrolysate (LOMAX et al., 1991). Formations of cellobiose can occur through dimerisation of the levoglucosan or as product from the active cellulose in Shafizadeh's scheme (LIU et al., 2008).

Based on aforementioned Shafizadeh model and propositions of POUWELS et al. (1989), shown in Figure 2.8. A number of probable reaction pathways for low molecular volatile products from cellulose through random homolytic and heterolytic fragmentations have been proposed by other workers (BOON et al., 1994; BREMER, 1991).

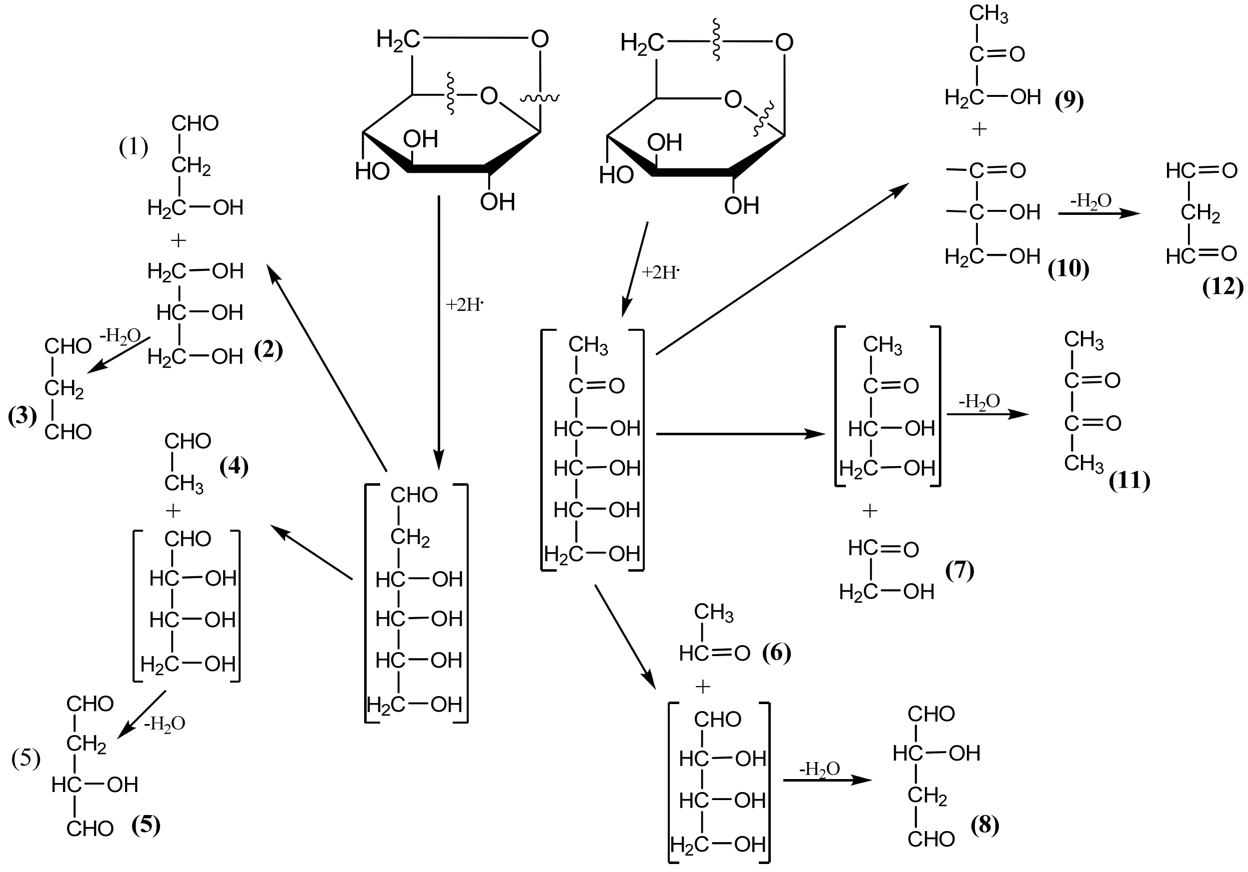


Figure 2.8: Possible intermediates and reaction pathways for small pyrolysis products from levoglucosan (POUWELS et al., 1989).

Key: **(1)** 3-hydroxypropanal; **(2)** 2,3_dihydroxypropanal; **(3)**, propanedialdehyde; **(4)** acetaldehyde; **(5)** 2-hydroxybutanedialdehyde; **(6)** acetaldehyde; **(7)** hydroxyacetaldehyde; **(8)** 2-hydroxybutanedialdehyde; **(9)** hydroxypropanone; **(10)** 2,3-dihydroxypropanal; **(11)** 2,3-butanedione; **(12)** propanedialdehyde.

Many authors have disputed the formation of cellulose derived volatile products been entirely through levoglucosan (PONDER and RICHARDS, 1993; RICHARDS, 1987). For instance, RICHARDS (1987) and BOON (1994) opined that the formation of hydroxyacetaldehyde, one of the major chemicals found in pyrolysates, could occurred through reverse aldolisation of depolymerised cellulose, parallel to the formation of levoglucosan as shown in Figure 2.9. Other possible products through this process include acetaldehyde, acetol, furfural etc.

Notwithstanding, these views do not eliminate the correctness of the Shafizadeh models. It can be said that the emergence of many volatile products from cellulose, just like in the entire lignocellulose, probably occur through homolytic and heterolytic decomposition reactions, but with some few predominant reaction in each case, depending on the reaction conditions.

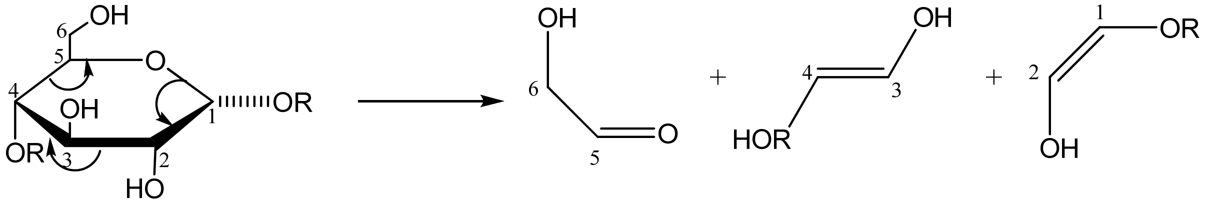


Figure 2.9: Formation of hydroxyacetaldehyde via 2+2+2 cyclo-reversion of cellulose (BOON et al., 1994)

The scheme depicted in Figure 2.10 illustrates reaction mechanisms for the production of cyclic compounds (furans and pyrans) from other anhydrosugars, as proposed by POUWELS et al. (1989). However, most of these reaction pathways largely remain unverified through reaction mechanism studies and provide vague explanation on the formation of gases such as CO and CH_4, which are clearer in the work of SHAFIZADEH (1982).

The mechanism of formation of hemicellulose derived products may not be substantially different from that of cellulose, save difference occasioned by high degree of polymerisation and crystallinity in the latter. A number of mechanisms speculated by some authors support this assertion (BREMER, 1991; SHEN et al., 2010a). Acetic acid is a major pyrolysis product found in the pyrolysis oil of xylan rich lignocelluloses such as hardwood and annual plant residues (straw). It is produced from the fragmentation of acetyls attached to the o-acetyl-xylan units (SHEN et al., 2010a). However, this product has also been detected as a decomposition product of cellulose following the rehydration of ketene from hydroxyacetaldehyde (PONDER and RICHARDS, 1993).

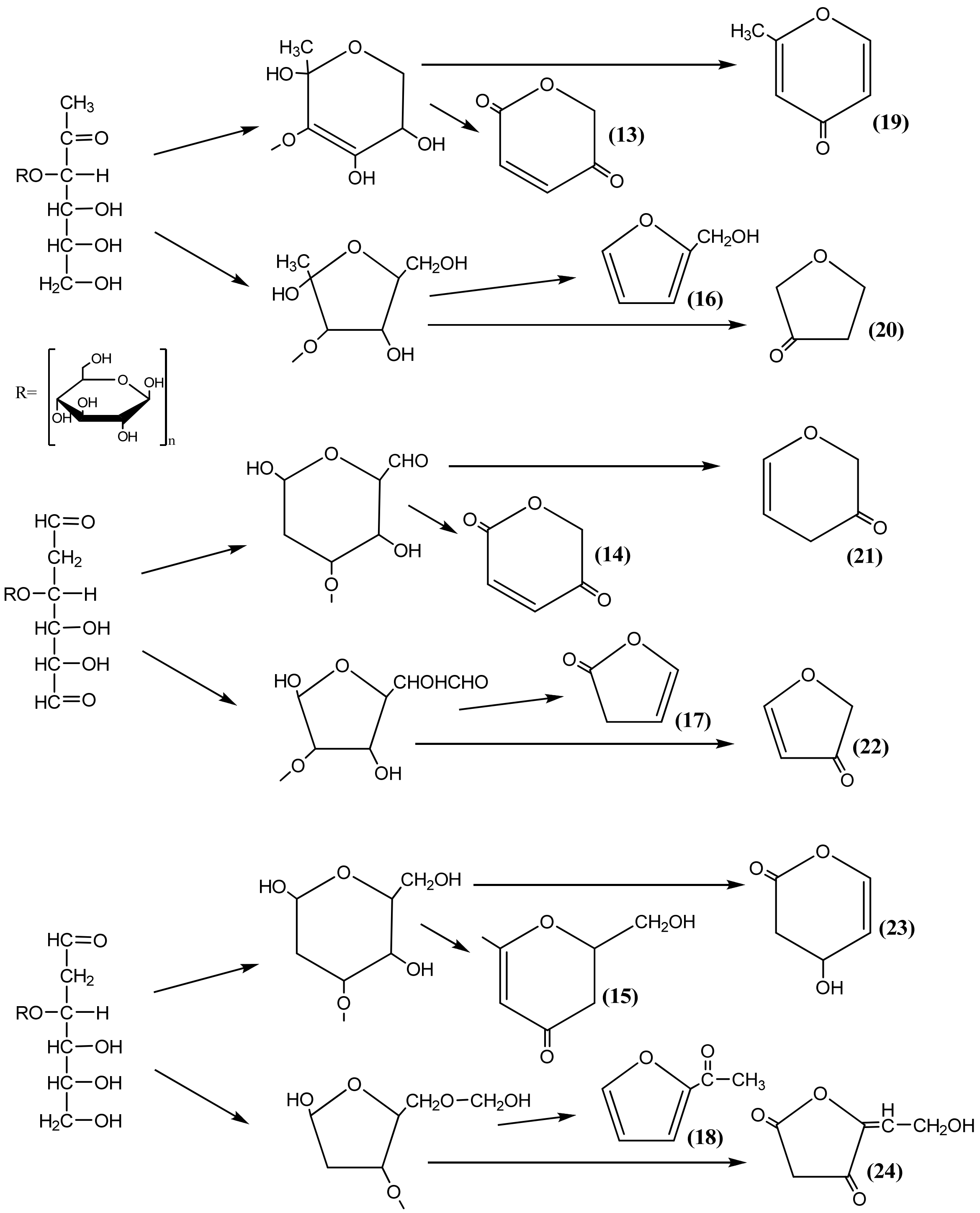


Figure 2.10: Possible routes for the formation of furans and pyran derivatives from anhydro-oligosaccharides (POUWELS et al., 1989).

Products: **(13)** 3.4-dihydropyran-2,5-dione; **(14)**=**(13)**; **(15)** methyl-formyl-(4H)-pyran-4-one; **(16)** 2-(hydroxymethyl)-furan; **(17)** (3H)-furan-2-one; **(18)** (5-)acetyltetrahydrofuran-2-one; **(19)** 3-hydroxy-2-methyl-(4H)-pyran-4-one; **(20)** tetrahydrofuran-3-one; **(21)** 2,4-dihydropyran-3-one; **(22)** 2,4-dihydropyran-3-one; **(23)** 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one; **(24)** 5-(2-hydroxyethylidene)-(5H)-furan-2-one.

High content of acetic acid in xylan rich lignocellulose may implies the predominance of its formation through the peeling off reaction. Other products obtainable from the pyrolysis of xylan include acetaldehyde, formic acid, propionaldehyde, methanol, and 2-furaldeyhde (SHAFIZADEH et al., 1972). According to BREMER (1991), the formation of 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one, as one of the main products from xylan could emerge through the pathway depicted in Figure 2.11.

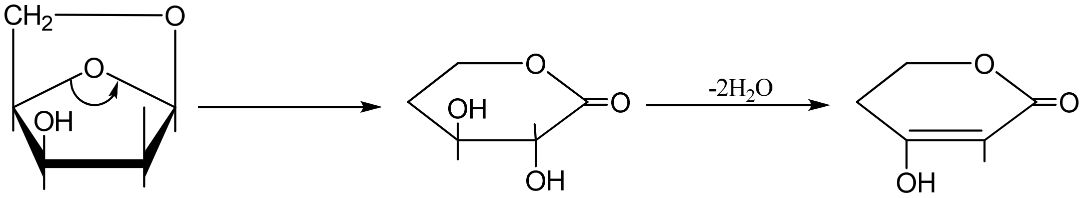


Figure 2.11: Formation of 4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one from 1,5-Anhydro-β-D-xylofuranose (BREMER, 1991).

The formation of water (known as reaction water) found in BCO has being attributed to intermolecular dehydration resulting in the formation of chains linked by ether groups and inter-chain cross-linking (RADLEIN et al., 1991).

2.2.1.3 Reaction mechanisms of lignin

The mechanism of reactions leading to the production of lignin derived pyrolytic products is more complex than that of polysaccharides. This is due to the numerous bonding forms that exist in the three dimensional heteropolymer. This reason partly explains the difficulty in arriving at a general reaction pathway for lignin by researchers. The difference in lignin constituents of different type of woods is another possible cause. Lignin pyrolytic degradation products consist of various phenolic compounds with different substitutions. These products emerge, following the thermal rupture of α- and β-alkyl-aryl ether bonds in lignin. The production of high amounts of monolignols has been attributed to the predominance of bond cleavage at the β-O-4 linkages in the macromolecule (KLAP et al., 1998; SAIZ-JIMENEZ and DE LEEUW, 1986).

Various chemical events during the decomposition of lignin against temperature profile as outlined by VORHER (1976) are shown in Table 2.2. It is presumed that homolytic fragmentation is mostly responsible for the fragmentation than heterolytic fragmentation since the former requires lesser energy for the fragmentation reaction (VORHER, 1976).

Table 2.2: Overview of chemical events against temperature gradient during pyrolysis of lignin (VORHER, 1976).

Temperature [°C]	Chemical events	Product
up to 175	Structural changes such as contraction and compression due to abstraction of water molecule	Water
175-250	Cleavage of β-, aryl- and alkyl ethers Intra molecular dehydration	Lignin fragments Water
250-300	Rupture of substituent with α-Hydroxyl- and Carbonyl groups at C_α- und C_β-atom positions	Phenols, aldehydes, aliphatic products
300 – 330	Cleavage of substituents (without reactive groups) at C_α- und C_β- group and on aromatic ring	Phenols and aliphatic products
325 – 330	Cleavage of C-C Commencement of condensation and polymerisation of fragmented products	Phenols and oligomers
330 – 400	Attainment of main phase of pyrolytic decomposition; Demethoxylation & fragmentation of phenylpropane continue; Formation of pyrolysates products through re-coupling of radicals; Stability of some linkages: biphenyl (up to 385°C), phenylcoumaran and resinol (up to 400°C)	Phenols, aliphatic products, neutral fractions, organic acids, gas and residue
From 400	Stabilisation of the degradation rate and Formation of stable structures	as above
From 600	Formation of char from residue and Further degradation of volatile products	Char Gas

Using lignin model substances, a number of authors have suggested that homolytic free-radical mechanism and intensive 6-centre retro-ene are involved in lignin thermal degradation (AUTREY et al., 1991; PETROCELLI and KLEIN, 1984; VAN DER HAGE et al., 1993). A modified representation of these mechanisms presented by VAN DER HAGE et al. (1993) is shown in Figure 2.12.

The production of phenol-, cresol- and catechol-type aromatic compounds result from secondary fragmentation of the primary guaicyl and syringyl products through free-radical chain reaction (SHEN et al., 2010b). The demethoxylation of the original moiety precedes the emergence of these products (Amen-Chen et al., 2001). On the source of dimeric and oligomeric lignin derived products in pyrolysates, owing to the free radical reaction pathway, decomposed products can react with one another to form dimeric and polymeric products. In contrary, van der Hage et al. (1993) noted that the higher thermal stability of aryl-aryl, aryl-alkyl and alkyl-alkyl bonds with respect to ethers bonds preserved part of the original lignin. This explains the detection of phenylcoumaran (β-5 linkage), phenylcoumarone (β-5 linkage), biphenyl (5-5 linkage) and resinol (β- β linkage) structures in the pyrolysis products.

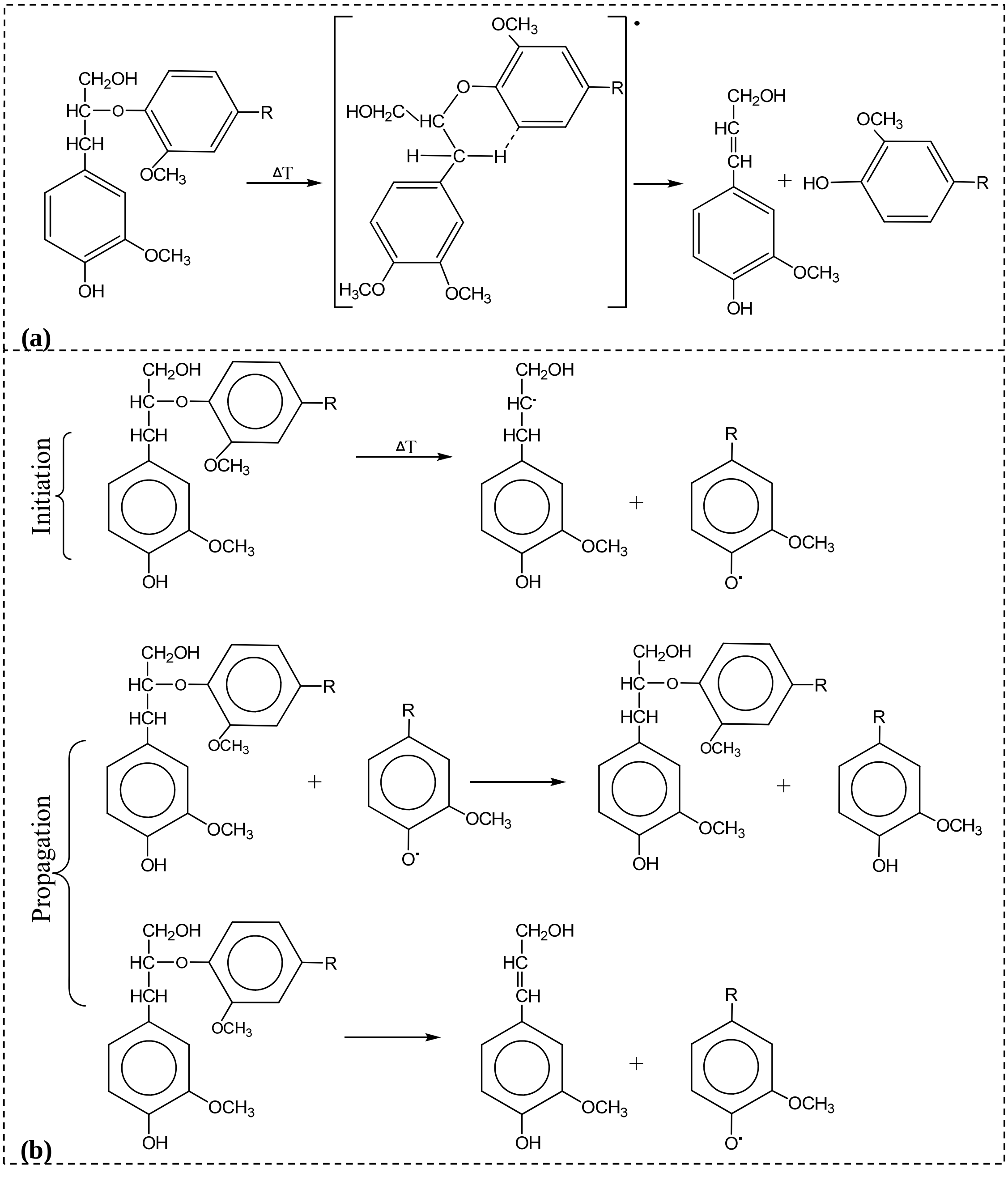


Figure 2.12 : (a) Free radical (b) free radical and concerted 6-centre retro-ene thermal degradation pathways of β-O-4 linked lignin structures (van der Hage et al., 1993)

2.2.2 Fast pyrolysis liquid product from lignocellulose

There are basically three main products obtainable from fast pyrolysis of lignocellulose namely; a liquid product, a mixture of non-condensable gases (such as CO_2, CO, methane etc.) and char. The liquid product is a dark brown mixture of over 300 condensable organic chemical products in varying proportions (CZERNIK and BRIDGWATER, 2004). It has numerous synonyms, which include bio oil; pyrolysis oil; bio crude oil (BCO), wood oil, pyrolysate oil etc. BCO is formed following a rapid cooling of the intermediate products obtained from pyrolysed lignocellulose. It is a single phase organic product, especially when obtained from bark-free woody biomass. On the basis of dry feedstock, BCO made up 60-75% average yield. Owning to high metal contents in annual plants such as grasses, its pyrolysis liquid yield is found between 55 and 60 wt. % on a dry basis (BRIDGWATER, 2011). And the product often consists of two phases (tar and liquid). In case of woody biomass, the liquid yield can be up to 75%. Char and gases from conversion processes account for 10-15% and 15-20% respectively. Most ash content of original feedstock is partitioned in the char fraction.

2.2.2.1 Factors affecting the bio crude oil yields and compositions

The yield and composition of BCO depends on factors such as feedstock type and operational parameters. Variations in the constituents of original feedstocks usually reflect in the yield and composition of their BCOs. Comprehensive compositional description of BCOs from different feedstocks have been carried out by previous authors (DEMIRBAS, 2007a; DEMIRBAS et al., 2004; MOHAN et al., 2006; MULLEN et al., 2009a; OASMAA et al., 2010).

Pyrolyses of different lignocellulosic feedstocks have revealed close relationship between organic products and constituents of the original materials. The chemical composition of BCOs obtained from softwoods always contains no traces of syringyl related products as expected. The lignin macromolecule of softwoods is basically made up of guaiacyl units. Likewise, the xylan content in hardwoods and many annual plants often results in corresponding acetic acid content in their BCO.

Considering the result of BA et al. (2004), high carbon and low oxygen contents was found in the vacuum-pyrolysis of softwood bark unlike the usual reported values in BCO from bark-free lignocellulose. High extractive content in the bark is a possible reason for this difference as indicated by relatively high viscosity of 62 cSt (at 50°C) and high calorific heat value of 27.9 MJ/kg.

In another investigation, feedstocks such as *Pterocarpus indicus, Cunninghamia lanceolata, Fraxinus mandshurica* and rice straw pyrolysed in a fluidised-bed reactor at optimum temperature of 500°C revealed that *Pterocarpus indicus* produced the best BCO on the basis of yield, heating value and low water content (LUO et al., 2004). The BCO contained mainly furfural, phenol, 2-methyl, phenol, 2, 4-dimethyl levoglucosan, vanillin, and furan-2-one.

In the work of other workers (YANIK et al., 2007), BCOs were obtained from three agricultural waste namely corncob, straw and *oreganum* stalk using a bench scale continuous fluidized bed. The products were fractionated into water soluble and pyrolytic lignin fractions. The results showed varying concentration of main pyrolytic products such as acetic acid, hydroxyacetaldehyde and acetol. Several other feedstocks including nuts and seed, algae etc. have been pyrolysed by other authors (DI BLASI et al., 1999; OASMAA et al., 2010; SENSOZ and ANGIN, 2008; TSAI et al., 2007).

However, the main goal of most trials is to find feedstock, whose BCO meets better quality and essential criteria as fuel product. Consequently, less attention has been paid to adjudging them on the basis of their chemical compositions suitability for chemical production. Among several factors that affect BCO yield and composition, feedstock properties with respect to ash content is viewed to have dominant effects (FAHMI et al., 2008). High concentrations of alkali and alkaline earth metal (potassium and calcium) are ubiquitous in lignocellulose. And these metals have catalytic effect on products of pyrolysis processes. However, their catalytic effects on the composition of liquid products vary (KEOWN et al., 2008; RAVEENDRAN et al., 1995).

BRIDGWATER (1996) observed that BCO yields can be controlled through conversion process parameters such as temperature, heating rate and vapour residence time. For instance, improvement in the heating rate combined with short residence time of the vapour maximise the gas and the liquid products. Typical organic yields from various lignocelluloses and temperature dependence of Poplar-Aspen are depicted in Figure 2.13.

The influence of temperature is one of the most investigated of these parametric factors. Detailed information of this can be found in numerous published works by various authors (ATES and ISIKDAG, 2008; DEMIRBAS, 2004, 2007a; GARCIA-PEREZ et al., 2008a; WESTERHOF et al., 2009). Effects of these parameters are not limited to just the yield but also affect the overall chemical composition of the product. Garcia-Perez et al (2008a) observed increase in the presence oligomers in BCO obtained at temperature above 350°C.

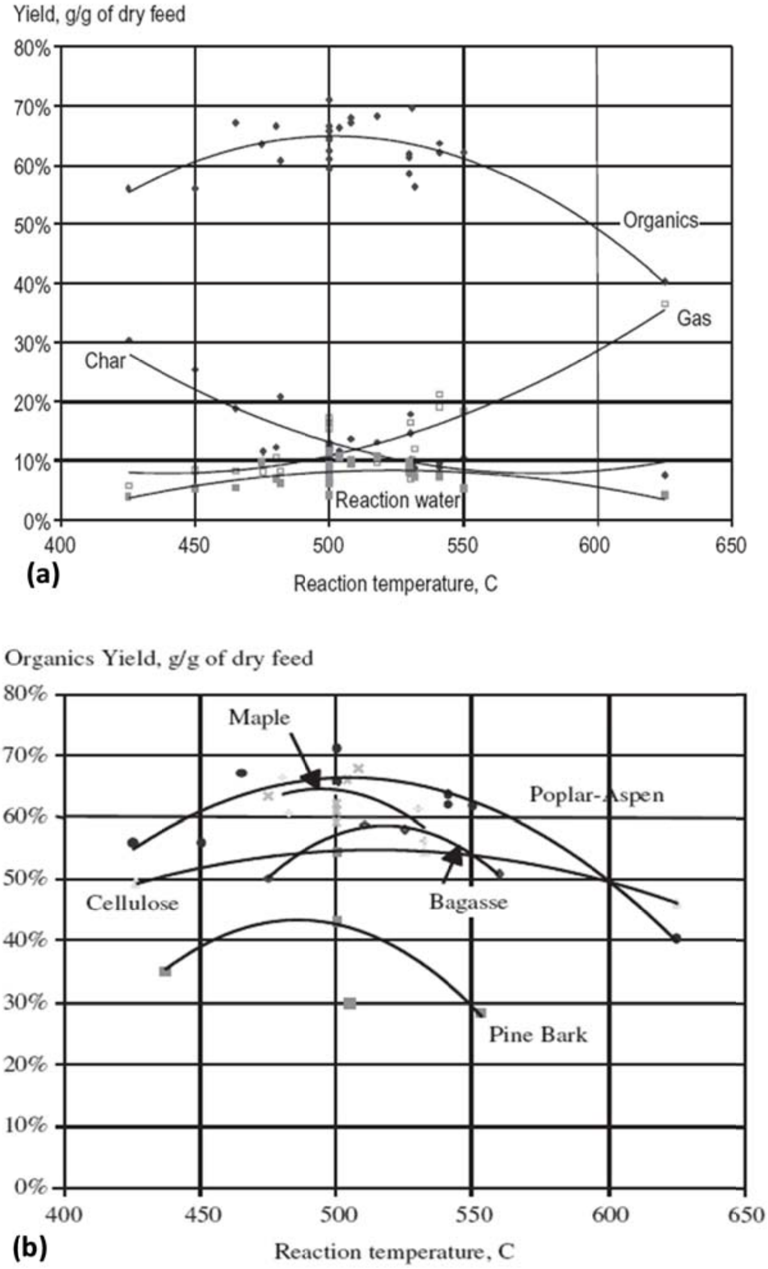


Figure 2.13: Effects of (a) temperature on pyrolysis products and (b) feedstock type on organic liquid yield (TOFT, 1998).

2.2.2.2 Bio crude oil characteristics

BCO is a free flowing highly oxygenated mixture. It has an acrid smoky odour due to the low molecular weight aldehydes and acids (BRIDGWATER, 2010). It has water content of ~18-30%, depending on feedstocks and conditions of pyrolysis. The water content is derived from the feedstock moisture and reaction water. This water is not readily separable from the mixture but a fraction of it can be evaporated using vacuum distillation at 30°C, giving a more viscous product. It functions to reduce the viscosity of the oil, but contribute to its poor lower heating value (LHV) and flame temperature (CZERNIK and BRIDGWATER, 2004). Water content in BCO is best determined using Karl-Fischer titration method (OASMAA and MEIER, 2005).

The organic liquid is slightly denser than water. It is miscible with methanol, ethanol and acetone but not with petroleum derived fuels. The elemental composition is comparable to that of original lignocellulose. Summary of some of its typical properties against heavy fuel oil are shown in Table 2.3. BCO has wide varying boiling points due to the presence of different volatile and non-volatiles like sugars and oligomeric phenols. The presence of these non-volatile components makes its distillation impossible beyond 250-280°C, leaving behind almost 35% residue as products of polymerization reaction (CZERNIK and BRIDGWATER, 2004).

Table 2.3: Physical properties of bio crude oil (BCO) and mineral oil

Properties	BCO	Heavy fuel oil
moisture content, wt. %	15-30	0.1
pH value	2.5-3.5	
elemental composition, wt. %		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
ash, %	0-0.2	0.1
HHV (MJ/kg)	16-19	40
viscosity @ 40°C, cP	35-1000	180
solid, wt. %	0.2-1.0	1
Density g/cm^3	1.19-1.28	0.93
distillation residue, wt. %	Up to 50	1
Pour point	-12 - -33°C	0.3

Modified data adapted from (CZERNIK and BRIDGWATER, 2004)

With oxygen content of 35-40 wt.% , almost the entire original oxygen content in feedstock is retained in different compounds found in BCO. This, in addition to water content, is responsible for the great difference in its heating value compared to that of hydrocarbons (<50 %). In addition, it contributes to the storage instability of the product (CZERNIK and

BRIDGWATER, 2004; OASMAA and CZERNIK, 1999). BCO can be stored for several years under normal storage condition without any substantial deterioration in its properties save increase in viscosity (BRIDGWATER, 2010). The presence of many organic acids such as acetic and formic acids put the pH of BCO around 2-3 and acid value of 50-100 mg KOH/g thereby making it corrosive to construction materials such as aluminium and steel. The oil is not corrosive to stainless steel metals (OASMAA and CZERNIK, 1999).

Over three hundred individual chemical components have been found in BCO (CZERNIK and BRIDGWATER, 2004; MOHAN et al., 2006). These chemical compounds can be broadly classified into acids, non-aromatic- alcohols, aldehydes and ketone, furans, pyrans, esters, sugars, benzenes, catechols, guaiacols (methoxy phenols), syringols (dimethoxy phenols) and lignin derived phenols. The largest fractions of these products are monomeric chemical products and decomposition fragments from lignocellulose macromolecules. The phenolic related compounds are fragmentation products of lignin. The relative amount of individual chemicals can be controlled through conversion parameters and catalysts. For instance, it has been noted that increased temperatures induce severe cleavage of alkyl groups on the aromatic products. The residual phenyl product condensed to form polycyclic aromatics (MOHAN et al., 2006).

2.2.2.3 Chemical characterization and fractionation of BCO

Complete chemical characterization of BCO remains hard to achieve, owing to the presence of high molecular products such as oligomeric non-volatile products, from both holocellulose and lignin macromolecules. The task is more cumbersome, considering intrinsic separation steps required to reduce the matrix effects from other components, before these heavy products can be properly characterized. A complete separation of a particular component of interest from over 300 compounds is very difficult.

Low molecular fractions in BCO consist of monomers that are identifiable through the use of gas chromatography (GC) fitted with appropriate column. The GC detectable fraction consists of volatile monomeric fractions from both holocellulose and lignin with medium polarity due to the presence of one or two hydroxyl units on the compounds. Three most prominent peaks in GC detectable monomeric fraction are hydroxyacetaldehyde, acetic acid and levoglucosan. These are holocellulose derived decomposition products. Hydroxyacetaldehyde is the highest individual fractions in BCO obtained from softwood and some annual plants. And acetic acid constitutes the highest fraction in xylan rich lignocellulose, such as hardwood and biomass from annual plants such as corncob. Many standard analytical methods for the characterisation of BCO have been developed and employed by many authors (BAYERBACH and MEIER, 2009; DAS et al., 2004; MULLEN et al., 2009b; OASMAA et al., 2003b; OASMAA and MEIER, 2005; OASMAA and PEACOCKE, 2001; SIPILA et al., 1998).

Means of separating BCO into different fractions is a vital requirement in order to recover various chemical products in it. Owning to the complexity of BCO composition (wide range of polarities and high content of oxygenated products) only solvent fractionation appears helpful in obtaining different fractions of the product. Several fractionating methods already developed for obtaining different fractions or a targeted fraction is well documented in several reviews (MOHAN et al., 2006; VENDERBOSCH and PRINS, 2010). The extraction scheme developed by Oasmaa et al. (2003a,b) is depicted in Figure 2.14. It enables the fractionation of different classes of organic compounds in BCO. Closely related to this scheme is the Brix method developed by the same authors for quick evaluation of BCO sugar content (OASMAA and KUOPPALA, 2008). They observed a good correlation between this method and sugar fractions obtained from the other solvent fractionation.

BCO can be fractionated into water soluble and water insoluble fractions under the action of highly agitated mixer (SCHOLZE and MEIER, 2001). The water insoluble fraction (residue after filtration and washing) is termed pyrolytic lignin (PL). This fraction largely consists of alkoxylated (poly-) phenyl compounds. The molecular size of this product has been determined to be around 5000amu (MOHAN et al., 2006). On re-pyrolysing, PL yielded monomeric phenolic products (BAYERBACH and MEIER, 2009).

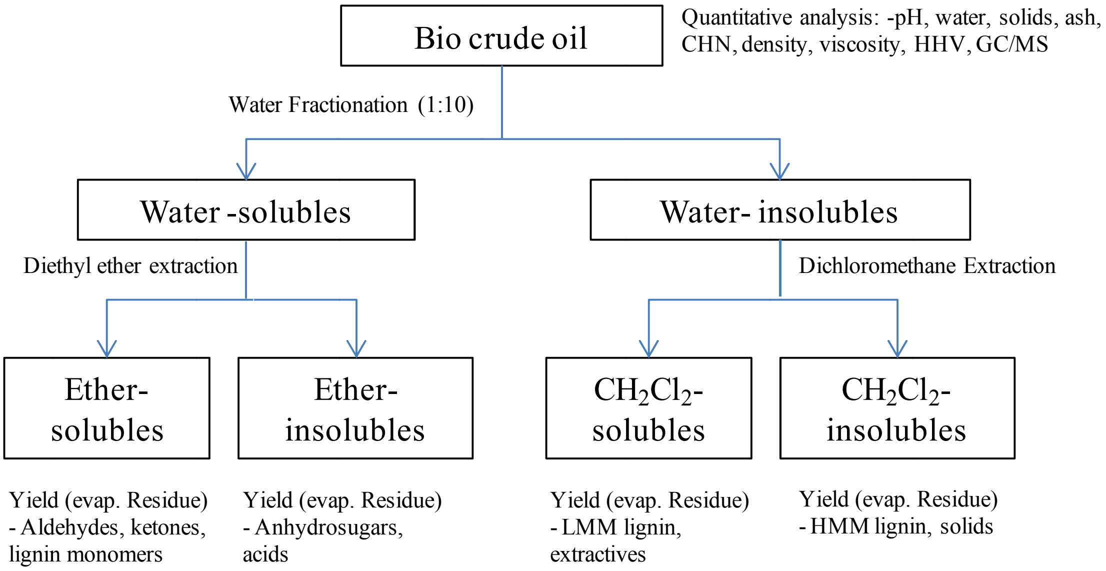


Figure 2.14: Fractionation scheme for BCO chemical characterisation (OASMAA et al., 2003a; OASMAA et al., 2003b)

Efforts to completely elucidate constituents of the pyrolytic lignin and some of the so called LC analysable monomers still remain a daunting task. Different modified forms of the fractionation method have been used by several workers for elucidating chemical constituents of BCO (BAYERBACH et al., 2006; SCHOLZE et al., 2001; SCHOLZE and MEIER, 2001). Based on this fractionation and chemical analysis, BAYERBACH AND MEIER (2009) have categorised BCO into four major fractions shown in Figure 2.15.

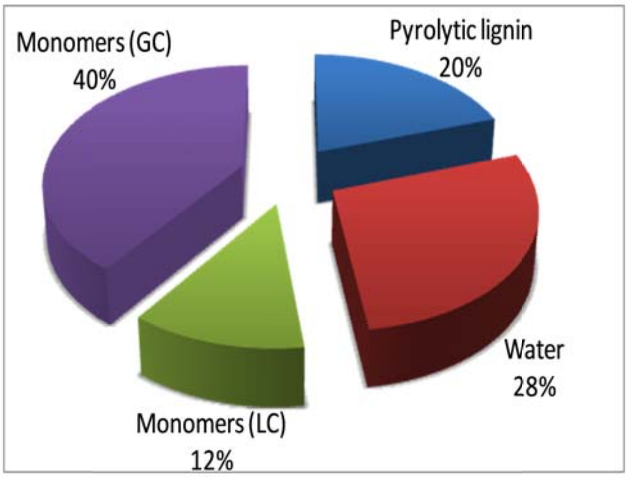


Figure 2.15: Distribution of BCO major fractions (BAYERBACH and MEIER, 2009).

Although few monomeric sugar decomposition products such as levoglucosan and other anhydrosugar sugars can be detected using GC, their peaks are often poorly resolved depending on the separation column and program. Some of these polar products, especially the dimeric and oligomeric components, can be better analysed through the use of high pressure liquid chromatography (HPLC). Their molecular size analysis is carried out using gel permeation chromatography (GPC). Substantial part of the fraction called monomers detectable by LC in the figure remains largely uncharacterised.

2.2.3 Chemicals in BCO

The heating of organic matter such as biomass in the absence of oxygen produces a mixture of gases, liquid and solid products. It is the only conversion path that offers the practicability of producing arrays of chemicals products via a single step conversion process. Pyrolysis liquid from slow pyrolysis process has served as a major source of chemicals such as methanol, acetic acid, turpentine and tars prior to the discovery of petroleum. Many companies like Chemviron (Germany) and Usine Lambiotte have obtained chemical products from the organic liquid in commercial quantity (CZERNIK and BRIDGWATER, 2004). Several more chemical products are produced via fast pyrolysis due to the fast rate of decomposition that generates numerous radical reactions (DIEBOLD, 1999). Chemicals produced from BCO have found applications as adhesives, resins, phenol, polyphenols, food flavourings, preservatives, slow-release fertilizers and deicers (BRIDGWATER, 2010).

BioLime is a BCO derived chemical product, developed by Dynamotive, for capturing SO_x emissions from coal combustor. The product can remove 90-98% SO_x from flue gases and destroy some nitrogen oxides. Also, the use of BCO as a substitute for creosote in wood preservation has been documented (CZERNIK and BRIDGWATER, 2004). A biodegradable slow-release nitrogen fertilizer has been produced from BCO reacted with $-NH_2$ groups (forming various imide and amide bonding). Slow degradation of the lignin helps to control soil acidity and improve the availability of phosphate (CZERNIK and BRIDGWATER, 2004; VENDERBOSCH and PRINS, 2010). Also, the use of the pyrolytic lignin as a replacement feedstock for the production of polymers and resins has been proposed (CHERUBINI et al., 2009).

One of the strategies required for the production of useful chemicals from biomass is the identification of products with substantial yields. So, the production of such chemicals can be optimised at the expense of other low-yield products through process parameters. Around 40 chemicals in BCO with highest individual yield ever reported have been selected and enumerated in Table 2.4. A full range of chemicals found in BCO have been enumerated in some published works (DIEBOLD, 1999, 2002).

Table 2.4: Chemicals in BCO ranked by their reported maximum yields

BCO, wt.%	Compound	Chemical group
0.9-13	Acetaldehyde, hydroxy-	Nonaromatic Aldehyde
0.5-12	Acetic acid	Acid
0.3-9.1	Formic acid	Acid
0.1-8.5	Acetaldehyde	Nonaromatic Aldehyde
0.7-7.4	Acetol (Hydroxypropanone)	Nonaromatic Ketone
0.1-7.2	Guaiacol, 4-propenyl-(trans) (Isoeugenol)	Guaiacol
0.1-5.2	Furanmethanol, 2- (furfural alcohol)	Furan
0.7-4.8	Syringol (2,6-dimethoxyphenol)	Syringol
0.9-4.6	Ethane, 1,2-dione (ethanedial; glyoxal)	Nonaromatic Aldehyde
0.1-3.8	Phenol	Phenol
0.1-3.3	Formaldehyde	Nonaromatic Aldehyde
0.6-3.2	Cellobiosan	Sugar
3.1	Anhydro-ß-D-glucofuranose, 1,6-	Sugar
0.7-2.9	Fructose	Sugar
2.8	Acetone	Nonaromatic Ketone
0.4-2.4	Methanol	Alcohol
0.1-2.3	Guaiacol, 4-propenyl-(cis) (Eugenol)	Guaiacol
0.3-2.2	5-(Hydroxymethyl)furfural (HMF)	Furan
0.7-2.0	Ethylene glycol	Alcohol
0.1-1.9	Benzene, 1,4-dihydroxy (Hydroquinone)	Phenol
0.1-1.9	Guaiacol, 4-methyl-	Guaiacol
0.1-1.8	Propanoic acid	Acid
0.1-1.5	Syringol, 4-propyl	Syringol
0.1-1.5	Syringaldehyde	Syringol
0.6-1.4	Ethanol	Alcohol
0.4-1.4	Anhydro-ß-D-glucopyranose, 1,6- (Levoglucosan)	Sugar
0.1-1.4	D-xylose	Sugar
0.1-1.3	Phenol, 2-ethyl-	Phenol
0.4-1.3	Glucose	Sugar
0.1-1.2	Furanone, 5-methyl, 2(5H)-	Furan
0.1-1.1	Guaiacol (Phenol, 2-methoxyl)	Guaiacol
0.1-1.1	Furan-2-one	Furan
0.1-1.1	Furaldehyde, 2- (furfural)	Furan
0.1-1.1	Benzaldehyde, 4-hydroxy-3-methoxy- (Vanillin)	Guaiacol

Modified data obtained from (BRIDGWATER, 2010; DIEBOLD, 1999)

Hydroxyacetaldehyde, acetic acid, hydroxypropanone, 3-hydroxypropanol, 5-hydroxy-2,3-dihydro-(4H)-pyran-4-one, 5-hydroxymethyl-2-furaldehyde, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one, 1,5-anhydro-fl-D-xylofuranose, levoglucosan are the most abundant compounds in the degradation mixture of lignocellulose (MEIER and FAIX, 1999). This list however excludes variations introduced by feedstock chemical composition. In which case, the content of products such as 1,5-anhydro-fl-D-xylofuranose is less significant when compared to other products. These products and some others not mentioned in the table like maltol have various industrial applications in food flavouring, preservatives, slow release fertilizer and hydrogen production etc.

Hydroxyacetaldehyde is found in high yield in BCO. This chemical, otherwise known as glycolaldehyde, has crucial application in food flavouring as the most active agent in liquid smoke for meat-browning, soft cheeses and tempeh. It can also function as precursor in the production of acetaldehyde. Furthermore, it is used as building block for several organic syntheses especially in the synthesis of heterocycles and imidazole. Patented methods have been developed by Red Arrow Product and RTI for the isolation of hydroxyacetaldehyde using crystallization (MAJERSKI et al., 2006; STRADAL and UNDERWOOD, 1995). The author equally noted that its production from lignin free feedstock is more efficient and economical.

Acetaldehyde is directly obtained in lignocellulose pyrolysis. Because of its volatility, large fraction of it escape with non-condensable gases but can be efficiently trapped in a gas washing bottle with water or in jacketed coil condenser at cryogenic temperature. It has found applications in paper and textile industries as crosslinker for starch based products. Here, it used as solubilizer and cross-linking agent. It can be added to ureas for wrinkle-resistant chemical treatment.

Levoglucosan (1,6-Anhydro-ß-D-glucopyranose) is one of most important cellulose derived products found in BCO. This chemical alongside with its chemically related product, levoglucosenone (1,6-Anhydro-3,4-dideoxy- ß-D-pyranosen-2-one), have been obtained with 46 and 26 wt.% yield respectively from cellulose (DOBELE et al., 2005). Both sugar anhydrides have potentials for the manufacturing of pharmaceuticals, surfactants and biodegradable polymers (CZERNIK and BRIDGWATER, 2004).

A number of process steps for the production of levoglucosan from lignocellulose such as pyrolysis, recovery and purification have been patented (SCOTT et al., 1995). With optimum pyrolysis temperature of 450-500, levoglucosan has been obtained from lignocellulose at high purity level (CZERNIK and BRIDGWATER, 2004). For instance, a yield of 43.3 wt.% of levoglucosan with purity level of 63% has been achieved (MEIER et al., 1997). Levoglucosenone can easily be isolated from BCO and has potential applications in pharmaceutical and food industry (AWAD et al., 2006; CZERNIK and BRIDGWATER, 2004).

The yield of levoglucosan in Table 2.4 can be adjudged underestimated when compared to values reported for different lignocelluloses (MULLEN et al., 2009a). It should be noted that the yields of these components depend on the type of feedstock and operation parameters employed in the production as well as the method of analysis. These reasons usually account for discrepancies in various reported yields from different authors. For instance, pyrolysis of beech wood at different temperatures has been shown to widely affect the chemical composition of the resulting BCO. A difference of -8 and 5 wt.% for acetic acid and 1-hydroxy-2propane respectively were observed in BCO obtained at 350 and 600°C (DEMIRBAS, 2007b).

Furfural is a chemical of important industrial applications. It is used as solvent for resins and waxes. Its application as feedstock for a range of aromatic components in preservatives, disinfectants and herbicides (TURLEY, 2008). 5-(Hydroxymethyl)furfural (HMF) is also a major products obtainable from BCO. It can serve as a building block for a variety of useful chemicals such as dimethylfuran (DMF), 2,5-Furandicarboxylic acid, levulinic acid, aldehydes, amines and alcohols through a simple conversion route (BINDER and RAINES, 2009). Several carboxylic acids in BCO can be used as road and runway deicer, and as catalyst in coal combustion (VENDERBOSCH and PRINS, 2010). Acrolein is the simplest unsaturated aldehyde. It has found applications in the production of acrylic acid, acrylic acid esters, superabsorber polymers and detergents. This product is one of the numerous volatile products obtained from lignocellulose pyrolysis. It can also be obtained via glycerol conversion.

Even with popular interest for the recovery of these chemicals from BCO, challenges militating against its use as economic and viable substitute for petroleum based chemical, is the difficulty in obtaining many of the chemical components in high yield and their low purity. In order to meet high quality for end-use either as fuel or chemical product, different approaches have been adopted to improve the yield and nature of chemical products in BCO. Some of these approaches, which include the use of catalyst, feedstock pre-treatment and BCO fractionation and upgrading, are briefly discussed below.

2.2.3.1 Catalytic modification of BCO

The application of catalysts in fast pyrolysis processes offers means of altering pyrolytic products. If properly engineered, yields of specific products can be enhanced at the expense of others. Catalytic pyrolysis has been widely employed to improve BCO properties. Numerous investigations have been carried using different types of catalyst (HORNE and WILLIAMS, 1995; IOANNIDOU et al., 2009; SHARMA and BAKHSHI, 1993; WANG et al., 1995). And comprehensive discussions on several catalytic upgrading options are detailed in many review articles (BRIDGWATER, 2011; MOHAN et al., 2006). Commonest amongst catalysts so far employed are various modified and unmodified zeolite because of their selectivity on various high molecular products in BCO.

Pyrolysate of high aromatic content and biologically active polynuclear aromatic (PAH) products was obtained from catalytic pyrolysis of pinewood in a 100-cm- high fluidised bed reactor using ZSM-5 zeolite catalyst (WILLIAMS and HORNE, 1994a). The product was largely deoxygenated when compared to the trial without catalyst. The authors observed that oxygen atoms in many oxygenated compounds were mainly converted to water and oxides of carbon at low and high catalyst temperature. It was also noted that increases in PAH content and decreases in the concentrations of acids is proportionally related to the process temperature.

A 16 wt. % yield of hydrocarbons (containing 3% toluene) from biomass was obtained by other workers (FRENCH and CZERNIK, 2010). This was achieved with the use of nickel, cobalt, iron and gallium-substituted ZSM-5 in a semi-continuous flow reactor and the product was analysed using molecular-beam mass spectrometry (MBMS). The deoxygenation activity of the catalyst decreased with time, owing to catalyst deactivation, through coke formation on catalyst surface. In related development, the pyrolysis of spruce wood in the presence of Al-MCM-41 type mesoporous catalyst at 500°C resulted in the complete elimination of levoglucosan, whereas acetic acid, furfural and other furans were found as important holocellulose derived pyrolytic products (ADAM et al., 2005). There was a substantial reduction in the amount of high-molecular phenolic compounds which are basically lignin derived products.

Several other workers have demonstrated the post pyrolysis conversion of products in BCO for chemical modification (MATHEWS et al., 1985; SHARMA and BAKHSHI, 1993; WANG et al., 1997). In the work of SHARMA and BAKHSHI (1993), both BCO and its fractions were subjected to catalytic upgrading at the temperature of 340-410°C in a fixed bed microreactor using H-HZSM-5 catalyst. Their results indicate that between 76 and 83wt. % of distillates obtained were aromatic products. This output result was not however substantial, considering the fact that the said maximum distillate yield translated to less than 12% of the feedstock. Mathews et al. (1985) achieved a maximum conversion of 65% (by weight) of BCO to C_6-C_{10} hydrocarbons including benzene, xylene, toluene and other higher molecular aromatic fractions.

The production of hydrogen as a clean fuel from bio oil through reformation process is another interesting upgrading route that has been developed (KINOSHITA and TURN, 2003; SARKAR and KUMAR, 2010; YE et al., 2009). The production of hydrogen from renewable sources is a boost to current interest in fuel cell applications. Using an electrochemical catalytic reforming method, a group of workers have reformed BCO to produce hydrogen over a NiCuZn-Al_2O_3 catalyst (YE et al., 2009). The production was adjudged efficient even at low temperature of 400°C with a yield of 93.5%. Other catalytic modifications that have been employed to improve the quality of chemicals produced from lignocelluloses include hydrogenation or hydrodeoxygenation process (ELLIOTT, 2007; ZHANG et al., 2003).

2.2.3.2 Modification through metal ions and salts

The removal or addition of metal ions is a modification strategy that can be used to alter the composition of various chemicals obtainable from lignocelluloses through pyrolysis. Alkali and alkaline earth metals (AAEM) such as Ca^{2+}, K^+, Mg^{2+}, Na^+ ubiquitously present in lignocellulose are known to influence the mechanism of thermal decomposition via fast pyrolysis. They can dictate the fragmentation path of the macropolymer different from the usual depolymerisation route (DOBELE et al., 2005; PISKORZ et al., 1989; RICHARDS and ZHENG, 1991; SCOTT et al., 2001). Both potassium and calcium are present in large concentration while sodium, magnesium and other metals are normally lesser in concentration than aforementioned duo.

A high concentration of mineral contents in lignocellulose induces high char formation at the expense of volatile products (WILLIAMS and HORNE, 1994b). The removal of the indigenous AAEM has been suggested as a means of improving the volatile yield. SCOTT et al. (2001) have worked on the removal of AAEM from lignocellulose via ion exchange by washing with diluted acid and hot water. It was observed that the exchange process was rapid but more effective in the removal of potassium than calcium. Hot water washing also proves efficient in the removal of the indigenous metals. The difference in the yield and composition of pyrolysate obtained from both normal and deionised poplar is shown in Table 2.5

On the role of AAEM, it is considered that individual metals have specific effects on reaction mechanisms. In a study carried out on effects of both potassium and calcium on the pyrolysate using FTIR coupled to thermal balance, it was observed that potassium ion only acts as a catalyst in the formation of high concentration of acetic acid, formic acid methanol and oxides of carbon (PAN and RICHARDS, 1989).

In contrast, it was noted that chlorides of transition elements such as Fe^{3+} and Cu^{2+} increased the amount of levoglucosan in pyrolysate when the metals were impregnated on the woody biomass sample (DOBELE et al., 2005). They also observed the production of both levoglucosan and levoglucosanone by the action of $FeSO_4$, but concluded that the levoglucosan to levoglucosanone ratio was governed by the phosphoric acid concentration used in the pre-treatment step to remove the native metal ions.

Table 2.5: Fast pyrolysis of normal versus deionised poplar

	Feedstock value	
	Poplar	deionised poplar
yield, wt.% mf		
Gas	10.8	2.6
Char	7.7	5.4
Organic liquid	65.8	75.9
Product water	12.1	14.0
Recovery, %	96.5	97.9
Liquid component, wt.% mf		
Levoglucosan	3.0	17.1
Other anhydrosugars	5.7	6.7
Hydroxyacetaldehyde	10.0	2.0
Acetic acid	5.4	1.3
Glyoxal	2.2	2.7
Pyrolytic lignin	16.2	22.4

(SCOTT et al., 2001)

3 Result and Discussion

This chapter presents overall summary and discussions of results, obtained from the research work. The presentation contains published results in three peer review articles as well as unpublished results. The latter are fused together with related subsections, under which different publications are discussed. Methods and experimental procedures employed in the work are detailed in related articles attached as Appendix 4.

3.1 Comparison of samples based on physicochemical analyses of pyrolysate obtained at optimum pyrolytic temperature (Publication 1)

One of the objectives of this research is to evaluate and compare chemical products obtainable from different lignocellulosic feedstocks. And central to this evaluation is the compositional analyses of feedstocks, prior to thermochemical conversion process. Substantial portion of results from these investigations have been published in publication 1 (AZEEZ et al., 2010). The publication also contains additional results, related to fuels properties of BCOs obtained from various feedstocks. Unpublished results not discussed in the publication are also discussed in this subsection.

3.1.1 Feedstock characterisation

The preliminary phase of this research work focused on the chemical characterisation of the raw materials. The raw materials are spruce (*Picea abies* L.), beech (*Fagus sylvatica* L.), iroko (*Chlophora excelsa* L.), albizia (*Albizia adianthifolia* L.), and corncob (*Zea mays ssp.*). This was followed by fast pyrolysis of original samples at optimum pyrolysis temperature of 500°C using a bubbling fluidised bed reactor. The obtained organic products were characterised and differentiated on the basis of their yields, chemical compositions and other characteristics.

The investigation of chemical composition of raw materials is considered an integral part of this research work, in order to deduce the influence of feedstocks on pyrolysis products. Various physico-chemical analyses of the five samples were carried out. These include moisture, ash, extractive contents and total metal analysis, Klason's lignin content and analysis of sugar. Standard analytical methods employed in these analyses and measurements have been discussed by AZEEZ et al. (2010)

Successive extraction was used to obtain various extractives fractions. The solvent employed were petroleum ether, acetone, and methanol:water (70:30, v/v). The summation of the various fractions makes up the total extractive content. The result of the extraction analysis is depicted in Figure 3.1. From this result, it can be observed that all the lignocelluloses contain low amounts of petroleum-ether extractable constituents. The relative amounts of this fraction in European samples were slightly higher than amounts found in lignocellulose of African origin. The African biomasses are richer in total extractives compared to European samples. Highest fractions of lipophilic and hydrophilic constituents were found in acetone extracts. This fraction makes up 50-60% of the total extractives in both iroko and albizia.

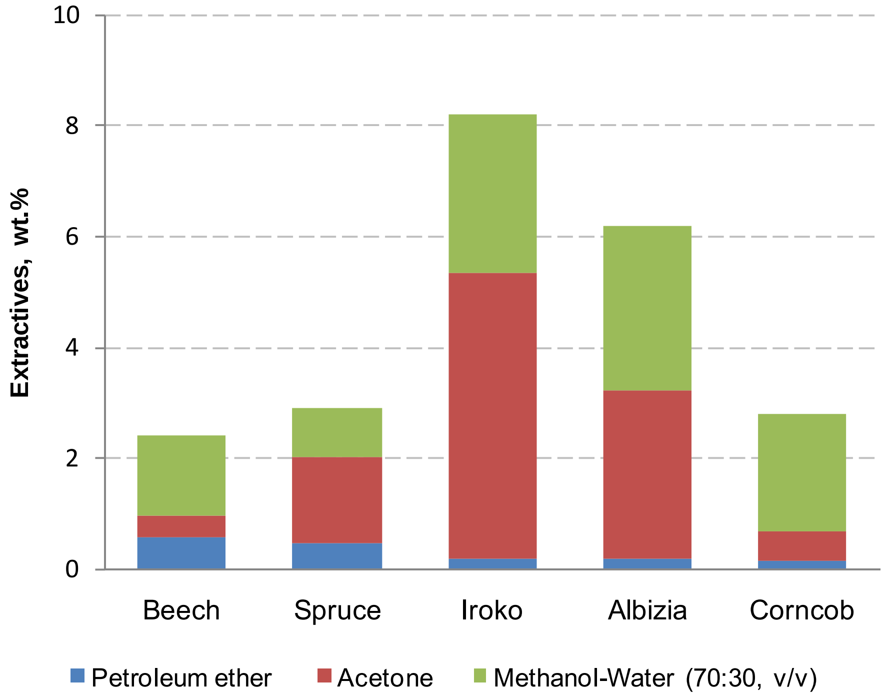


Figure 3.1: Different extractive fractions in raw materials.

In addition, acetone and petroleum fractions account for fatty acid alcohol, waxes, sterols, fats, steroid esters and terpenoids in samples (CONNER et al., 1980). The combination of these fractions is higher in spruce than beech, but lower than amounts found in African hardwoods. The petroleum ether fractions in both European lignocelluloses double (at least) the concentrations in other biomasses. The methanol-water fractions in both iroko and albizia are darker in colour, probably indicating higher quantities of tannins and pigments. Tannins are various poly-phenolic substances found in lignocellulose extracts (BOUSTINGORRY et al., 2005). They are efficiently isolated from wood with polar extractant (ROWE et al., 1969). The similarity in amounts of methanol-water fractions in both woods and corncob is probably due to the relative ease of removing more glycosides and some monomeric and oligomeric sugars in the annual plant, thereby compensating for differences in other hydrophilic extractive components.

The analysis of polysaccharides in raw materials was carried out using High pH Anion-Exchange Chromatography (HPAEC-borate) with spectrophotometric detection at 560nm (PENG et al.; WILLFÖR et al., 2009). The result of analysed monomeric sugars revealed the dominance of glucose ranging between 40 and 48% in the extract-free samples of all raw materials. Looking at overall results of the component and ultimate analyses shown in Table 3.1, corncob is clearly distinguished from woody biomasses based on its xylose content, which doubles amounts found in hardwoods.

This observation coupled with the amount of other hemicellulose found in residual fractions (apart from arabinose) indicates that arabino-4-O-methylglucorono-xylan is the main hemicellulose in corncob, constituting about 33 wt.% of the feedstock. This gives a xylose and 4-O-methylglucoronic acid ratio of 77:1 compared to 12-18:1 and 7.3:1 in hardwood and softwood respectively. A definite conclusion on this ratio is hard to drawn. It is possible that xyloglucan, a form of glucan hemicellulose, slightly contributes to the high xylose content. Nevertheless, the production of chemicals from corncob would be markedly influenced by its xylose fraction. This is unlike softwood, wherein the monosaccharide plays a less significant role.

According to FENGEL and WEGENER (1984), estimates of cellulose in feedstocks can be deduced by adopting the rough approximation of 2:1 and 3:1 as maxima mannose to glucose ratios, for mannans in hardwood and softwood respectively, For example using this approximation, the contribution of glucose from the beech glucan is obtained as 0.7%. By deducting this from the total glucose, the amount of cellulose in beech is found to be 45.3%. In a similar fashion, amounts of cellulose in spruce, iroko, albizia and corncob are 43.1, 47.2, 45.1 and 40.3 wt.% respectively. This estimation is premised on the assumption that no contribution to the glucose content in the hydrolysate was made by glucans hemicellulose.

Table 3.1: Component and ultimate analyses of samples

Component analysis (wt.%)					
	Beech	Spruce	Iroko	Albizia	Corn cob
Extractives	2.4	2.9	8.2	6.2	2.8
Klason Lignin	21.8	29.0	26.2	25.2	19.0
Holocellulose	68.5	70.2	64.8	63.7	75.7
Glucose	46.0	47.4	48.2	45.7	40.4
Xylose	18.1	5.8	12.1	14.9	30.9
Mannose	1.4	12.9	2.0	1.3	0.1
Galactose	1.0	2.3	0.8	0.4	1.0
Arabinose	0.5	1.0	0.2	0.2	2.8
Rhamnose	0.5	0.2	0.5	0.3	0.1
Cellobiose	0.1	0.0	0.0	0.1	0.1
4-O-Methyl glucoronic acid	1.0	0.8	0.9	0.9	0.4
Ultimate analysis (moisture and ash free (maf.) wt. %)					
Carbon	46.9	48.3	43.9	46.4	43.6
Hydrogen	6.2	6.3	5.3	5.8	5.8
Nitrogen	0.3	0.4	0.4	0.6	0.7
Oxygen*	45.9	44.6	46.9	45.5	48.6
HHV *MJ/kg***	18.7	19.5	16.5	17.4	16.9
Ash content %	0.7	0.4	3.5	1.8	1.2
Moisture content %	9.7	8.4	9.4	9.7	9.7
Volatile matter, %	85.9	83.5	70.4	72.7	80.6
Fixed carbon, %	18.7	19.5	16.5	17.4	16.9

* By difference. ** Calculated according to Boie's equation.

However, it is well known that starch in forms of amylose and amylopectin (glucan hemicelluloses) are often present in parenchyma cells of wood tissue. Other glucan-type hemicelluloses in biomass include callose and laricinan (an acidic glucan). FENGEL AND WEGENER (1984) noted that another glucan with β-(1→3)- and β-(1→4)- linked glucose units in ratio of 1:1 to 1:2 has been found in plants such as wheat, maize and oats. Therefore, the use of this approximation to estimate cellulose in lignocellulose must be done with caution.

But, estimated values largely compare with amounts of cellulose in most angiosperm and coniferous woods. So, estimating cellulose through this method appears more reliable than the old gravimetric methods.

It can be observed from the result that beside glucose, mannose and xylose are found to be major monosaccharides in softwood and hardwood respectively. This perfectly agrees with the general trend on the composition of woody biomasses. The influence of other monosaccharides on pyrolysis liquid products may be limited, due to their low abundance in the original lignocellulose.

In terms of lignin content, spruce has the highest content among all samples (Table 3.1). Normally, the coniferous wood is richer in lignin than hardwoods (SJÖSTRÖM, 1993). The content in both African hardwoods is higher than beech. The residue obtained from the hydrolysis favourably compared with determined Klason’s lignin content for most lignocelluloses. Therefore, it offers a means of estimating lignin content in biomass with low mineral content.

The ash content of all samples was determined using the TAPPI Testing Method T211. The individual inorganic mineral constituents were determined using inductively couple plasma optical emission spectroscopy (ICP-OES), following a total digestion using microwave. It was noted that the lignocelluloses of African origin have higher ash content than both spruce and beech (Table 3.1). A detailed result of the metal contents is contained in publication 1 (AZEEZ et al., 2010).

The ash content of iroko is most remarkable, tripling total amount in both beech and spruce. Much of this difference arises from Ca^{2+}contribution, which constitutes over 60% of total inorganic mineral content in the wood. Similarly, potassium ion in all African lignocelluloses was found ten times its content in spruce. And the amount of aluminium in iroko, corncob and albizia is four times higher than the upper limit value (<50ppm) for elements classified as trace element in woody biomass. Both potassium and calcium are macronutrients essential for plant growth and constituent most abundant elements in woody biomass. The mineral content of lignocellulosic feedstock is an important parameter in thermochemical conversion owing to catalytic effects of the metals, which ultimately alter the reaction mechanisms and the composition of final products (PAN and RICHARDS, 1989; WILLIAMS and HORNE, 1994b).

3.1.2 Comparison of BCO of various samples

Feedstocks were subjected to fast pyrolysis at the optimum temperature of 465-475°C in a 300g/h fluidised bed reactor. Each feedstock was pyrolysed twice. Average material mass balances for duplicate trials are shown in Table 3.2 with relative standard deviation between 2-6% (calculated based on yields). The results show that the highest yield of BCO was obtained from beech and spruce while iroko gives the least pyrolysate with 50.6%. Detailed results of various physico-chemical analyses of the BCOs in relation to their fuel properties are contained publication 1.

Like other BCOs, the water contents of the oils range between 22.0% (in spruce) and 32.2% (in corncob). The amount in corncob is related to increased formation of pyrolytic water due to high xylose content in the sample. This pentose sugar appears to be less thermally stable than hexoses.

Table 3.2: Mass balances of samples fast pyrolysis*

	Beech	Spruce	Iroko	Albizia	Corn cob
Reactor temperature	465-470°C	465-470°C	465-470°C	465-470°C	465-470°C
BCO, *wt. %*	62.7	62.7	50.6	54.7	56.2
Condensate, *wt. %*	7.4	7.3	5.8	6.7	5.1
Total liquid product, *wt. %*	70.1	69.9	56.4	61.4	61.3
Organic**, *mf wt. %*	57.5	57.1	40.4	47.6	43.9
Gas***	22.6	23.0	23.1	24.3	27.2
Char, *daf. %*	10.2	10.1	22.8	16.6	14.7
Pyrolytic water, *wt. %*	9.7	9.8	13.3	11.2	14.0
Conversion-to-volatile, *wt. %*	88.7	86.7	77.5	83.3	83.6

* mean values of replicate pyrolysis trials are reported ** organic = (Bio oil + Condensate – bio oil water content – condensate water content) *** percentage by difference based on wet weight.

BCOs from various samples were characterised using GC/MS/FID, for the purpose of comparing their various chemical products. Over 80 chemical components were detected, which represent between 33-44 wt.% of the organic liquid. Detected chemical products are classified into major chemical groups, acids, non-aromatic aldehydes and ketones, furan, pyrans, sugars, benzenes, catechols, lignin derived phenols, guaiacols and syringols.

A comparison of 12 most prominent chemical products in various BCOs is shown in Table 3.3. A complete list of quantified components is shown in Appendix 1. From Table 3.3, the concentrations of most chemical products vary among feedstocks, but this do not substantially affect the physical appearance and fuel properties of the BCOs. The result (shown in Figure 3.2) reveals that holocellulose derived products are most dominant. It can be observed from the figure that acids, non-aromatic aldehydes and ketones constitute most abundant chemical products in all samples except in spruce, wherein the sugar fraction ranked next to non-aromatic aldehydes. These chemical classes consist of various products derived from the holocellulose.

The result also shows that lignin fractions are the least decomposed components among three classes of lignocellulose main components. This result reveals only components, which are detectable in GC. The nature of column used for the separation (middle polar) may cause elusiveness of some compounds to separation or detection.

Acetic acid makes up between 96-98% of the acids in all samples. The rest consists of formic and propionic acids. These acids are poorly separated on the intermediate polar column (Zebron ZB 1701) used for this analysis. Acetic acid is an important chemical with wide industrial applications. This product is formed during pyrolysis from cleaved acetyl groups, attached to the xylan units (in hardwood and in annual plants). BCO mainly derives its low pH value from acetic acid. It is observed that spruce contains the least amount of acetic acid, as a result of the absence of acetyl on its xylan. There are however few acetyl groups attached to carbons 2 and 3 of the hexose units in galactoglucomannan as previously mentioned. The amount of acetic acid in corncob (the highest among all samples) just like the hardwood is traceable to its xylose content. It has also been noted that the organic acid can be formed as fragments from both hexose and pentoses and from lignin components (BRANCA et al., 2003).

Table 3.3: Main products in BCO of various feedstocks.

Beech		Spruce		Iroko		Albizia		Corncob	
Compound	wt. %	Compound	wt. %	Compound	wt. %	Compound	wt. %	Compound	wt. %
Acetic acid	8.03	Acetaldehyde, hydroxy-	9.80	Acetaldehyde, hydroxy-	6.97	Acetic acid	6.79	Acetic acid	8.47
Acetaldehyde, hydroxy-	7.87	Levoglucosan	4.47	Acetic acid	6.09	Acetaldehyde, hydroxy-	6.65	Acetaldehyde, hydroxy-	5.05
Acetol	2.72	Acetic acid	2.49	Acetol	4.32	Acetol	3.08	Acetol	4.68
Levoglucosan	2.43	Acetol	2.42	Cyclopentene-1-one, 2-hydroxy-2-	1.36	Propanal	1.44	Phenol, 4-vinyl-	2.54
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	1.53	Pyran-4-one, 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	0.91	Propanal	1.29	Levoglucosan	1.39	Cyclopentene-1-one, 2-hydroxy-2-	1.92
Propionaldehyde, 3-hydroxy	1.44	Cyclopentene-1-one, 2-hydroxy-2-	0.89	Cyclopentene-3-one, 2-hydroxy-1-methyl-1-	1.11	Cyclopentene-1-one, 2-hydroxy-2-	1.24	Guaiacol, 4-vinyl-	1.70
Cyclopentene-1-one, 2-hydroxy-2-	1.19	Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	0.88	Anhydro-ß-D-glucopyranose, 1,6-(Levoglucosan)	1.09	Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	1.04	Propanal	1.37
Propanal	0.96	Propionaldehyde, 3-hydroxy	0.88	Propionaldehyde, 3-hydroxy	0.84	Propionaldehyde, 3-hydroxy	0.99	Cyclopentene-3-one, 2-hydroxy-1-methyl-1-	1.29
Furanone, 2(5H)-	0.59	Propanal	0.58	Anhydrosugar unknown	0.80	Furanone, 2(5H)-	0.64	Butanone, 1-hydroxy-2-	1.26
Furaldehyde, 2-	0.55	Guaiacol, 4-propenyl-(trans) (Isoeugenol)	0.50	Guaiacol	0.78	Cyclopentene-3-one, 2-hydroxy-1-methyl-1-	0.62	Levoglucosan	1.20
Cyclopentene-3-one, 2-hydroxy-1-methyl-1-	0.50	Vanillin	0.47	Furanone, 2(5H)-	0.72	Furaldehyde, 2-	0.59	Furaldehyde, 2-	0.95
Syringol	0.48	Furanone, 2(5H)-	0.46	Guaiacol, 4-vinyl-	0.71	Syringol	0.59	Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	0.92

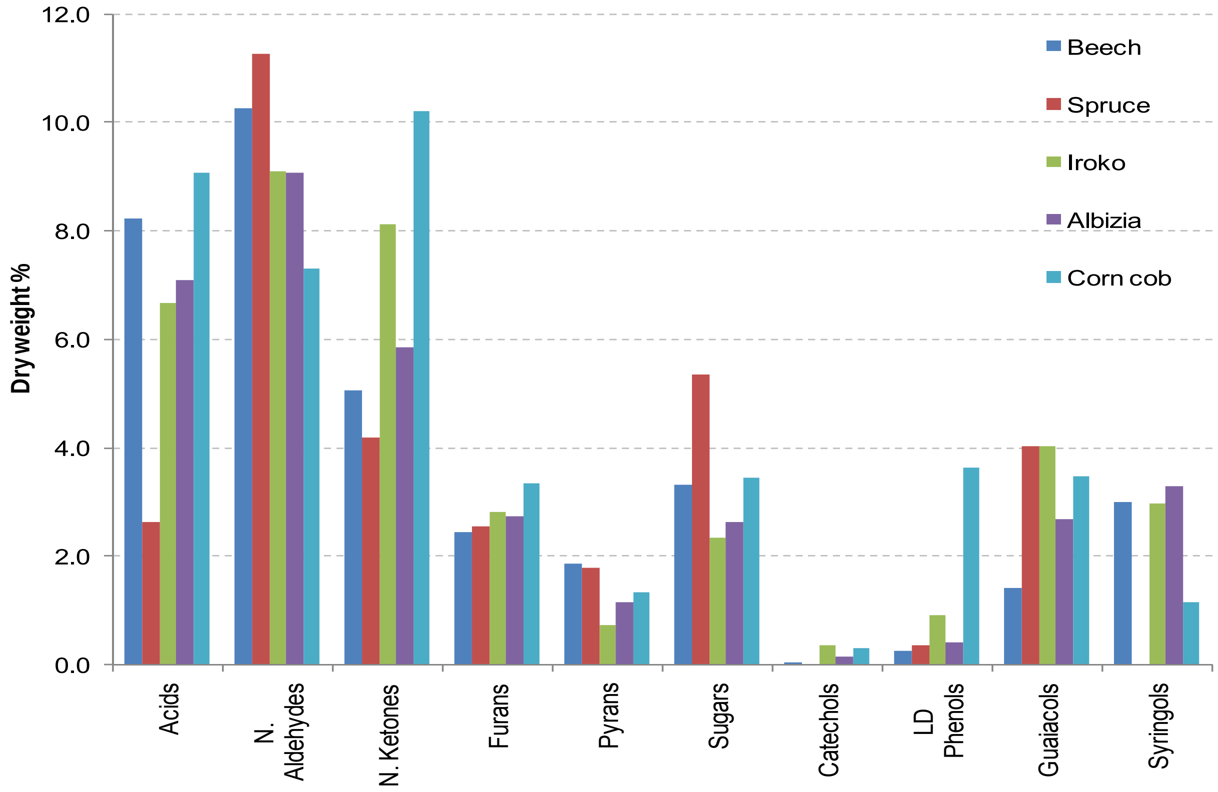


Figure 3.2: Classes of chemical products in BCO

Hydroxyacetaldehyde is another major constituent in BCO of all samples, ranking next to acetic acid in beech, albizia and corncob. It has the highest concentration in both spruce and iroko. Its concentration in iroko's BCO is not significantly different from amounts in other hardwoods. Its ranking in Table 3.3 is due to smaller acetic acid fraction in the sample compared to other hardwoods. Hydroxyacetaldehyde makes up between 5-10 wt.% in BCOs of investigated samples. It is a holocellulose derived chemical product. A competition between sugar rings fragmentation to form hydroxyacetaldehyde and depolymerisation of cellulose to yield levoglucosan via trans glycosylation reaction has been discussed by several authors (RICHARDS, 1987; SHAFIZADEH et al., 1979).

Levoglucosan (1,6-anhydro-ß-D-glucopyranose) constitutes the second main product in spruce. It maintains concentration favourably compared to amount in beech. However, this important pyrolysis product maintains a low concentration between 1.1 and 1.40 wt. % in all African lignocelluloses. Bearing in mind that the cellulose contents in both iroko and albizia is nearly equal to amounts found in European samples, it can be deduced that the decomposition pathways of cellulose to levoglucosan were altered by high mineral contents present in both biomasses.

It is interesting to note that corncob yields the highest amount of single lignin derived individual products among the samples, although it has the least Klason's lignin content. The amounts of 4-vinyl phenol and 4-vinyl guaiacol in this sample are (at least) 4 times and 3 times higher than any other lignin derived product in all samples. Considering the fact that corncob lignin structure contains the three lignin units, just like in hardwood, the proportion of some of these units in its biopolymer is suspected to be largely responsible for this discrepancy. The effect may be due to the type of bonding between different lignin building blocks in the sample. The presence of a high number of β-O-4 within the macromolecule (thermally labile) may limit the occurrence of free radical fragmentation reaction.

Acetol (hydroxypropanone) is another major chemical, whose formation is probably influenced by mineral content. This product has higher concentration in BCOs from all African lignocelluloses compared to European biomasses. A similar trend was observed in case of propanal, which constitute between 1.3-1.4 wt.% in BCOs obtained from African biomasses. Both products are carbohydrate derived chemicals. Other products, such as 2-hydroxy-2-cyclopentene-1-one, 3-hydroxy propionaldehyde and 2(5H)-furanone, are found in BCOs without substantial difference in their quantities among all samples. In addition, 1-hydroxy-2-butanone and 2-furaldeyhde (furfural) are present in large amounts in corncob pyrolysate. The concentration of the former is at least three times higher in corncob compared to other lignocellulose. Both chemicals are formed as decomposition products from holocellulose. The suggestion of furfural being is a pentose derived product by DEMIRBAS (2007b) appear weakened by the concentrations of this product in various BCO compared to the proportion of arabinose and xylose in original samples. The observation agrees with the result obtained from the pyrolysis of cellulose and different hemicelluloses by BREMER (1991), which revealed the presence of furfural in all samples. This product could have been formed from the decomposition of both pentose and hexose sugar.

As previously mentioned, only about 40% of the BCO products can be effectively quantified on GC/MS. The characterisation of the remaining products is often done qualitatively owning to the complexity of the mixture, resulting in poor resolution. The matrix effects from other products usually hinder the effective separation of solutes of interest. For instance, the BCO of beech was fractionated into water soluble and insoluble fractions followed by a clean-up of the former through solid phase extraction (using C18 bed) and the eluate was subsequently freeze-dried to obtain a syrup-like product. A 2mg/ml solution of the syrup and some sugar and anhydrosugar standards were injected in HPLC 1100 fitted with a RHM Rezex column and UV and RID detectors. Only very few sugar peak were effectively resolved as shown in Figure 3.3.

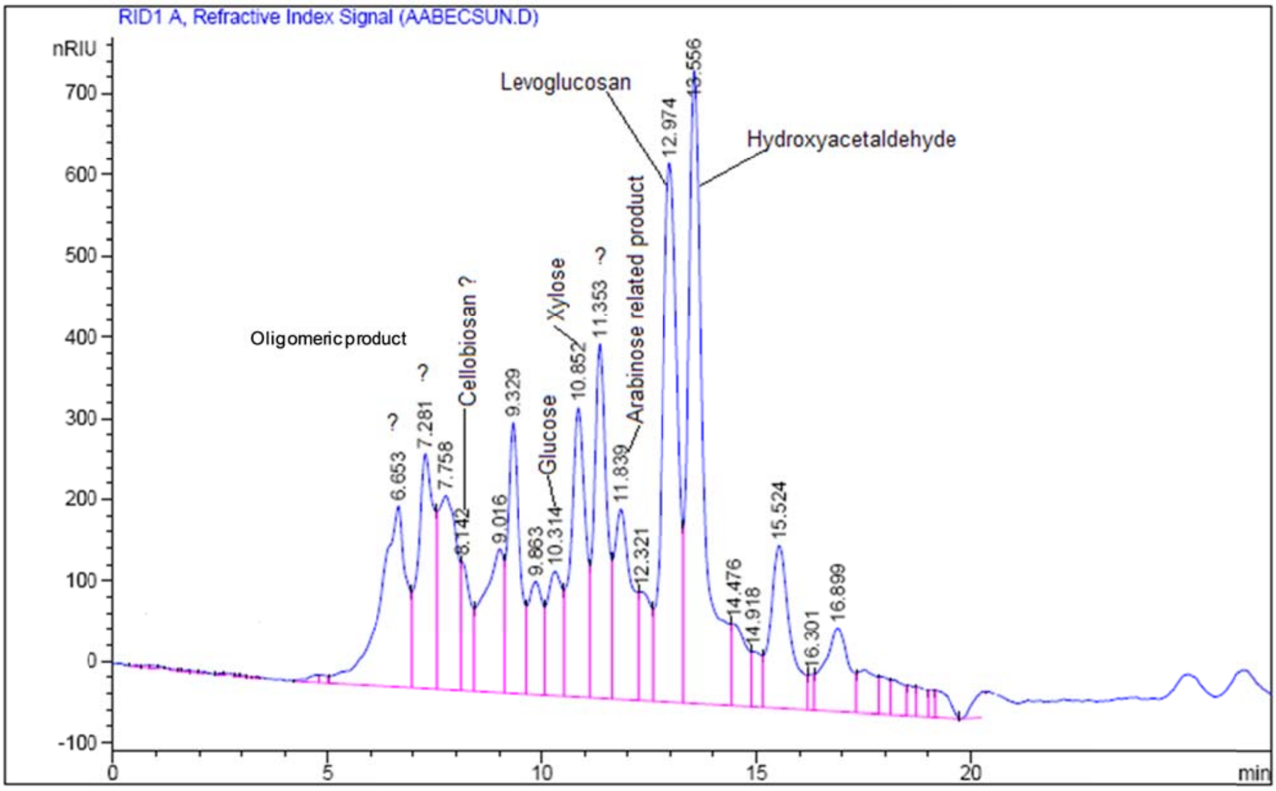


Figure 3.3: HPLC result of BCO water soluble fraction

The result reveals the presence of levoglucosan, xylose and small concentrations of glucose and arabinose related product. However, the detection of many non-sugar (but polar) compounds such as hydroxyacetaldehyde and some unidentified peaks with poor resolution illustrates the complexity of this fraction. Based on aforementioned works of Shafizadeh, it can be inferred that this fraction largely contains various decomposed polysaccharides ranging from monomeric to oligomeric products.

Some low volatile chemical products, produced from fast pyrolysis of lignocellulose, usually escape along with non-condensable gasses owning to their volatility and molecule size. In order to identify such products, condensable gasses were collected as condensate from gasses leaving the electrostatic E-filter with the aid of double jacketed condenser at -30°C. This product contained between 64-77% water as determined using Karl-Fischer titration method. Chemical characterisation of the condensate fractions carried out using head space gas chromatography fitted with both mass spectrometer and flame ionisation detector (HS-

GC/MS/FID) on a HP INNOWAX column revealed varying fractions of volatile chemicals products. A look at the result depicted in Figure 3.4 shows dimethoxy methane, acetaldehyde, 2,3-butanone, methyl alcohol and propanal as the main products in most samples.

However, some of these volatile products were elusive to detection when the same condensates were analysed on Zebron ZB 1701 column, an optimum column used for BCO analysis. The result from this analysis, shown in Figure 3.5, reveals that 8 – 19 dry weight % of the fraction consist of acetic acid. Other major compounds found in the fraction are acetol, acetaldehyde, furfural and several ketone products.

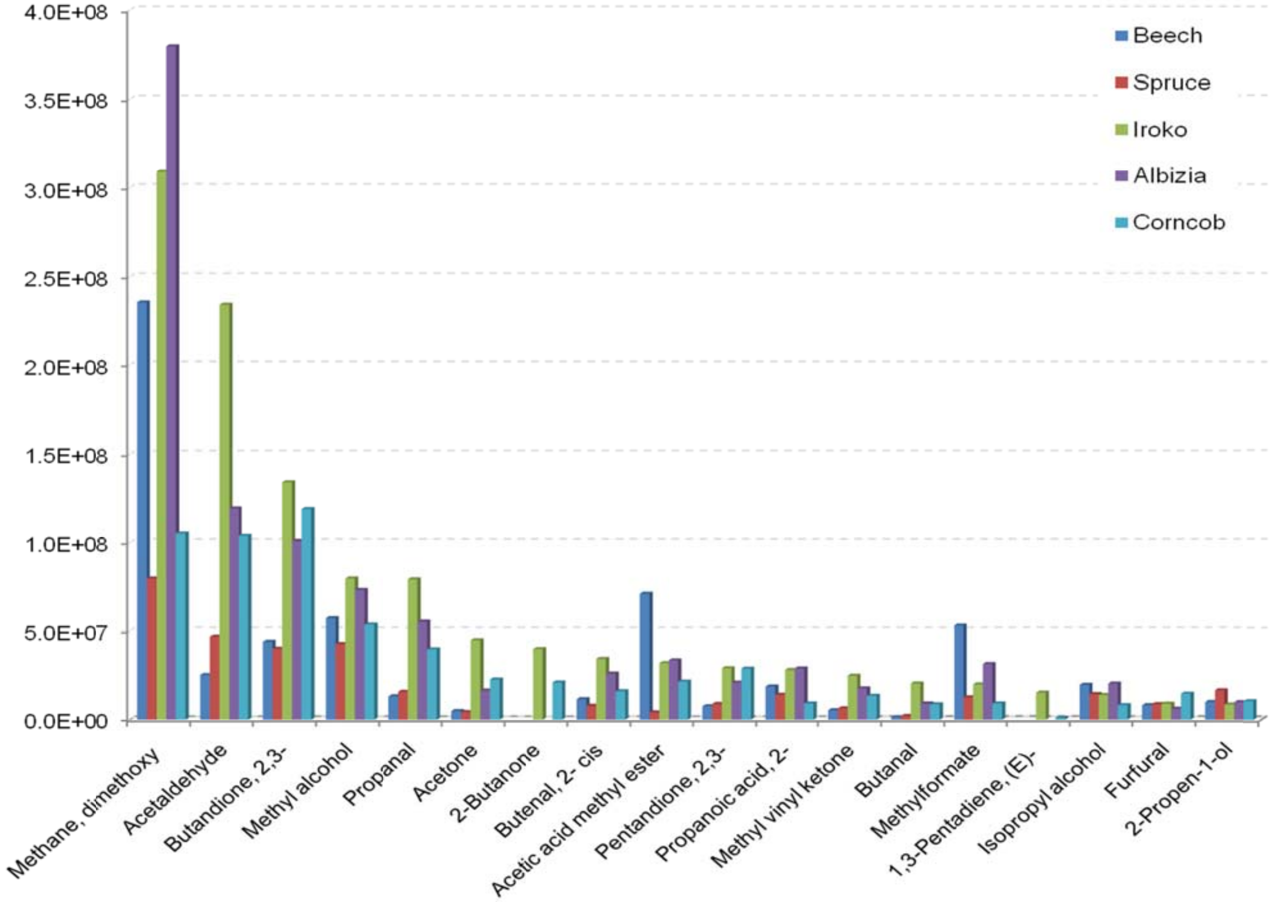


Figure 3.4: HS-GC/MS/FID of condensate fraction

To study the molecular distribution of chemical products in BCO, samples of various BCO were prepared in dimethyl sulfoxide and analysed using gel permeation chromatography (GPC) with both UV and RID detectors. The result of the analysed shown in Figure 3.6 indicates that the molar mass polydispersity indices (obtained as D=M_w/M_n) range from 12.8-16.4, minimum and least values obtained from corncob and iroko respectively. The ratios are largely influenced by molecular fractions whose molar masses are smaller than 106g/mol (the least molar mass in our calibration standards).

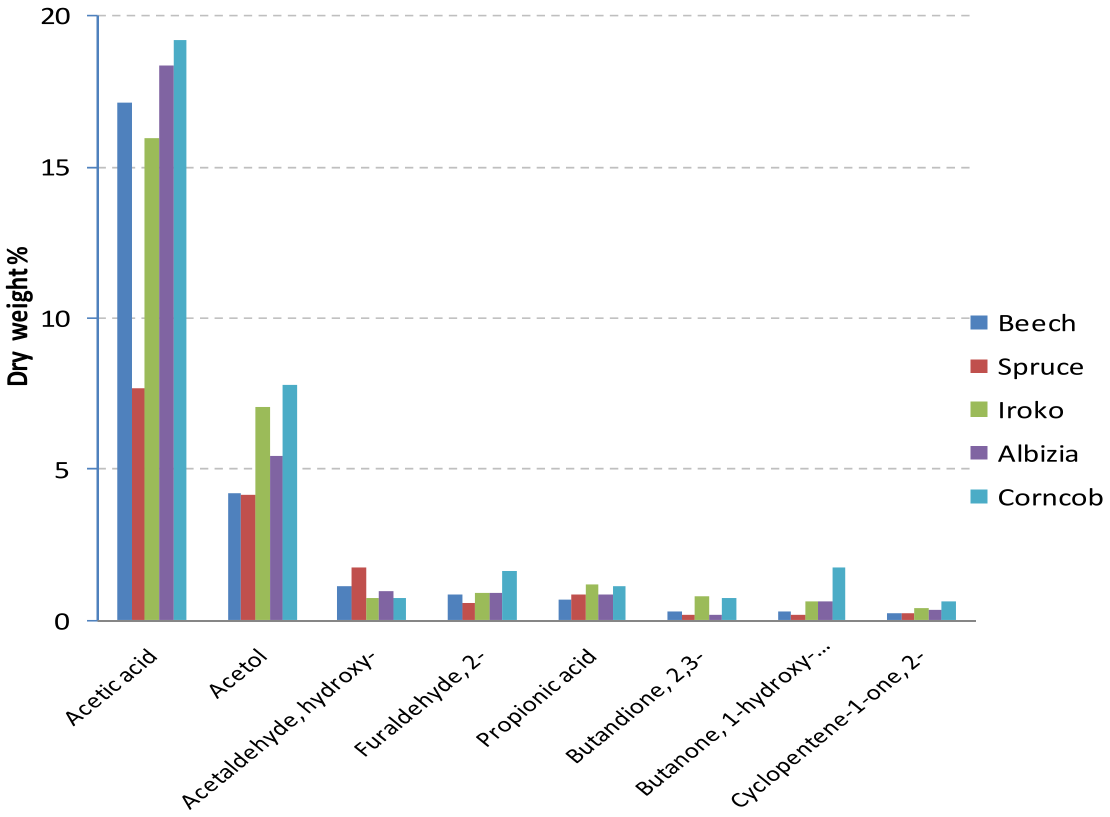


Figure 3.5: Major chemicals in condensate fraction detectable using GC/MS

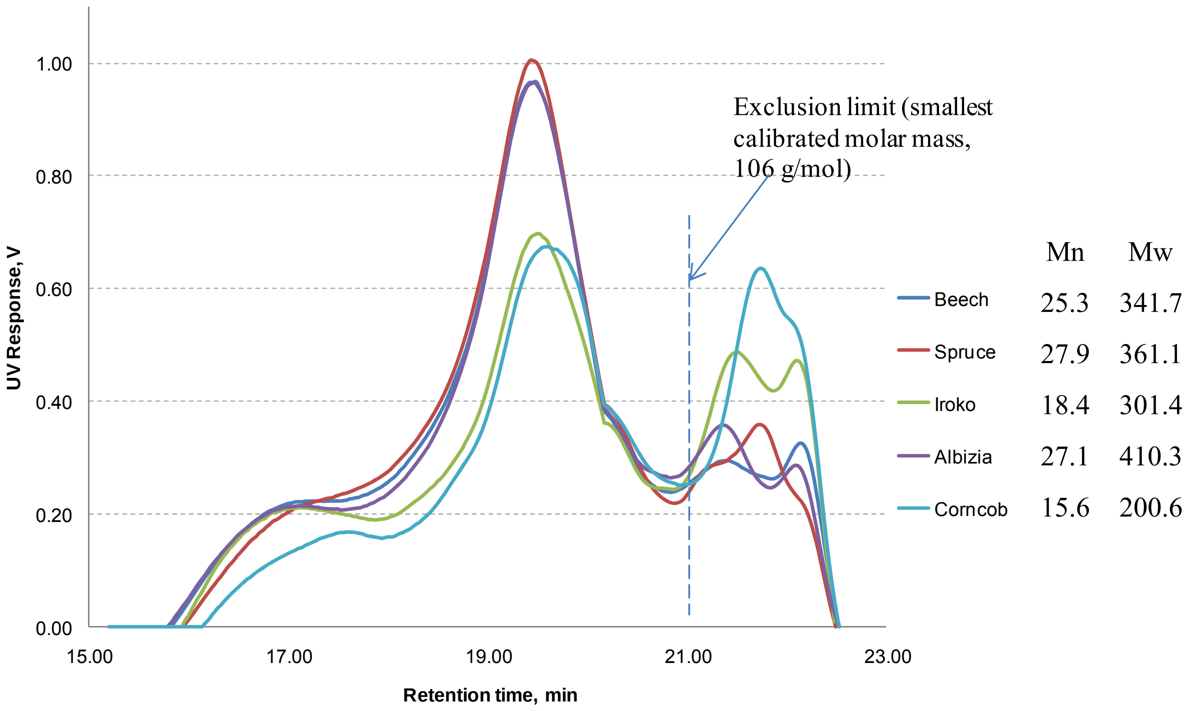


Figure 3.6: GPC plot of samples' BCO

In conclusion, there are distinct differences in the chemical composition of BCOs from different lignocelluloses, which reflect the dissimilarities in chemical compositions of feedstocks. Comparison of BCOs from similar wood type (for example iroko, albizia, and beech) indicates no substantial difference among products' chemical groups. However, high metal content in African biomasses, especially the hardwood, could make them less attractive feedstock for chemical production. Conversion process modification will therefore be required to improve their product yields. The role of high extractive content in yields and quality of products from these feedstocks appear less important, based on average uniformity in the physical quality of various BCOs. The nature of the corncob biopolymer structure makes it an ideal lignocellulose feedstock for chemical generation via thermochemical conversion. Its pyrolysis produces better yield of individual valuable chemical products with less severe random fragmentations of the macromolecules.

3.2 Influence of temperature and removal of indigenous minerals on pyrolytic chemical products (Publication 2).

The basic principle of pyrolysis involves the decomposition of organic matter via heat in an inert environment. This partly explains why temperature and heating rate play important roles in the nature of pyrolysis products. For instance, on the basis of differences in heating rates, fast pyrolysis produces several products not present in slow pyrolysis products. This subsection explains effects of temperature and feedstock pretreatment on decomposition behaviours of different samples and chemical composition of their pyrolysate.

3.2.1 Thermogravimetric (TG) analysis of samples

To understand the decomposition behaviour of different samples, thermogravimetric analysis of all samples were carried out using a TG 209 F1 Iris thermal analyser. The analysis was run between 300-700°C at a heating rate of 10°C/min in nitrogen environment. An overlay of TG curves (shown in Figure 3.7a) reveals that the major decomposition step started at around 220°C in all sample. Before this degradation phase, less than 3% weight loss was recorded, except in iroko with slightly higher mass change. It is worth of mentioning that little mass losses due to moisture elimination were observed at this stage owning to the fact that samples were vacuum-dried over phosphorus pentoxide prior to analysis. The first order differential plot (DTA) obtained (see Figure 3.7b) reveals a minor decomposition peak around 150-190°C only in iroko. This mass loss probably resulted from the thermal decomposition of certain thermal labile components from the extractive-rich African biomass. The small peak due to moisture elimination across all samples can also be seen on the DTA plot between 3 and 5 minutes after the commencement of the analysis.

With increased temperature, decomposition of corncob spanned the narrowest temperature range (220-400°C) within which two distinct decomposition events occurred. This accounts for about 64% total mass loss. The decomposition in this region is very rapid considering the inclination of the profile. This is ascribed to loss of hemicellulose and some cellulose in biomass (SONOBE et al., 2008). However, juxtaposing this profile with that of beech shows decomposition of higher fraction in beech (71%), although, the holocellulose content in the former is 8% higher than the latter. This observation may be due to the morphology of corncob and possible effects of its mineral contents (such as potassium), which is four times higher than that of beech. A similar conclusion can be deduced for two other African biomasses with minimum mass change in this region (iroko-51%; albizia-59%). It is obvious from the DTG curves that beech and spruce produce more volatiles products at the rate of 18%/min compared to African lignocelluloses.

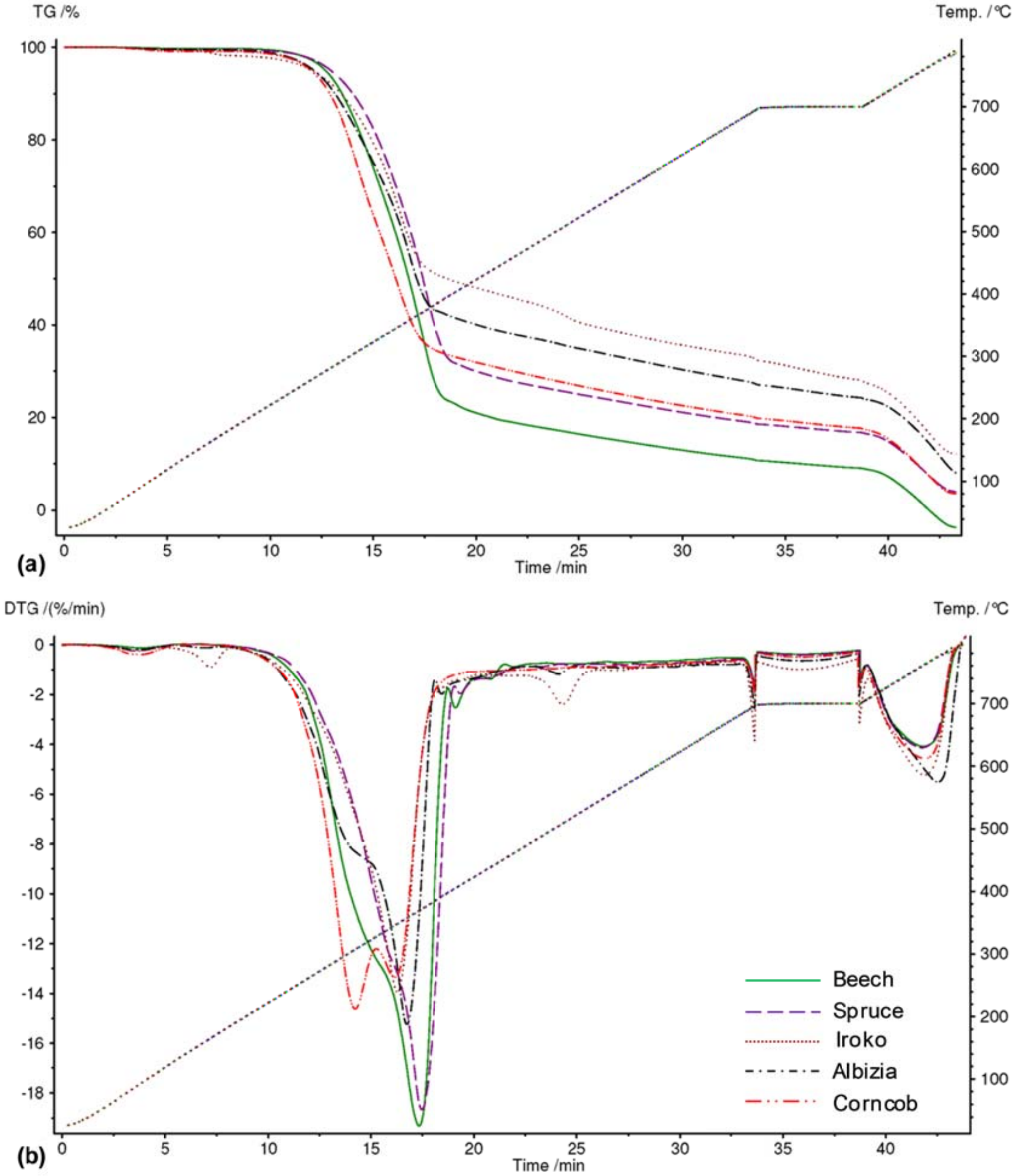


Figure 3.7: Overlay of thermograms from beech, spruce, iroko, albizia and corncob.

The high hemicellulose content in corncob accounts for the distinct peaks in its decomposition profiles. The first part (220-330°C) represents hemicellulose decomposition phase while the effect between 330 and 400°C is due to cellulose and partial decomposition of lignin (SONOBE et al., 2008). This suggestion is strengthened by the pattern of the peak and high de-volatilisation rate compared to iroko with the least hemicellulose content. The first peak is sparingly observed in iroko.

Following main de-volatilisation stage, the thermal profiles of all samples appear similar. It can be inferred that the composition of residues at this stage is fairly uniform, except in case of iroko with irregular decomposition profile. In other samples, a less inclined decomposition gradient between 420-700°C corresponds to further de-volatilisation of lignin and (possibly) decomposed cellulose. The result agrees substantially with reports of earlier workers on the thermal behaviour of different biomass components (CHEN et al., 2003; VENDERBOSCH and PRINS, 2010).

However, a definite decomposition profile for lignin is difficult to obtain. VENDERBOSCH and PRINS (2010) have observed, there are usually overlaps in the decomposition temperatures of lignocellulose main components. It would be seen in subsection 3.2.1.2 that the decomposition of some lignin fraction even starts at temperatures as low as 300°C. Some authors have however suggested that decomposition profiles of whole biomass samples can be derived from the summation of thermal behaviours of their main components (NAVARRO et al., 2009; RAVEENDRAN et al., 1996).

The residues left after the third de-volatilisation phase minus the ash content represent the fixed carbon in various samples. These values are shown in Table 3.1 with iroko and albizia maintaining the highest values of 26.1% and 25.5% respectively. More volatiles are released from the two European feedstocks than African feedstocks with volatile matter found to be 85.9% and 83.5% for both compared to 70.4%, 72.7% and 80.6% for iroko, albizia and corncob respectively.

3.2.2 Analytical pyrolysis at different temperatures

This subsection focuses on the study of effects of temperature on yields of individual chemical products in pyrolysate. The evaluation of influences of some pretreatment options such as water and acid washing as well as the reintroduction of selected metal ions (impregnation) in washed sample was also carried out. Pyrolyses of the prepared samples were carried out using an analytical pyrolysis unit (Py-2020iD micro-furnace pyrolyser) fitted on a GC/MS/FID. This system was chosen for the study based on positive correlation between its chromatogram and those obtained from BCO from GC/MS. In addition, Py-GC/MS enables the identification of other products such as propanal-2-one (methylglyoxal), butandione and indenes that are rarely detected in BCO due to their low concentrations and volatility. The system therefore enables 1-step identification of all volatile products. Major products already noted in previous sections and other new products at high temperatures were identified. Rather than the absolute concentration, peak areas of identified products from the FID signal were used for evaluation, owing to the difficulty in calibrating Py-GC/MS.

Principal component analysis (PCA) of pyrolysis data obtained for beech products over the whole temperature range is shown in Figure 3.8. It accounts for 96% of the validated variations in tested sample. The delineations of PC1 and PC2 are based on yields of individual chemical products.

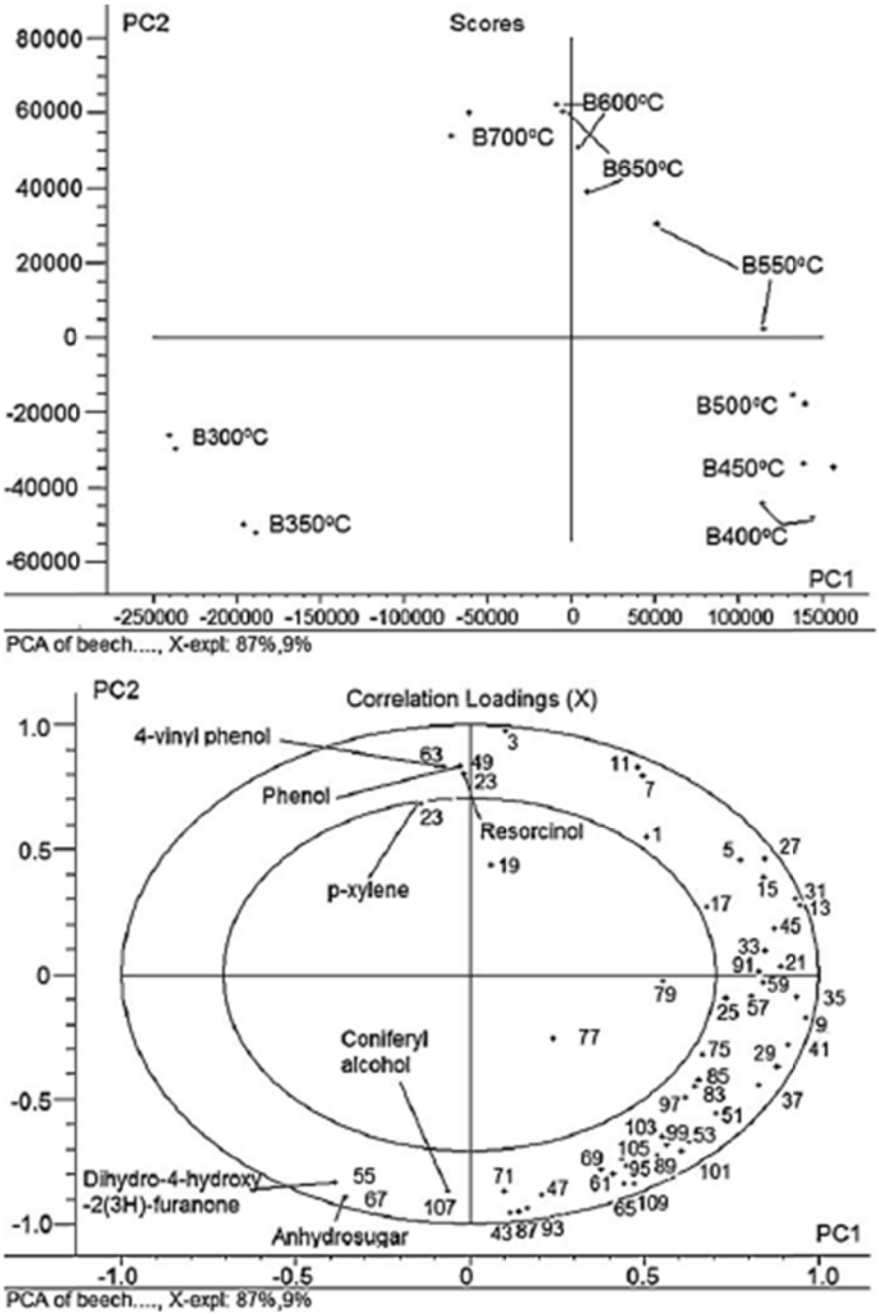


Figure 3.8: PCA scores and loadings of beech pyrolysis products at 300-700°C

The PCA indicates that pyrolysis at 300-350°C just like 650°C-700 produces the least yield of individual pyrolysis products. There are limited reaction pathways for the formation of volatiles at low temperature. And at high temperature, severe fragmentation of macromolecules occurs with possibility of multiple reactions to produce small amount of individual volatile products. Most of these products are non-aromatic aldehydes and ketones. Also, thermal labile products from both polysaccharides and lignin will decompose to non-condensable gases such as CO, CO_2, and CH_4 (SONOBE et al., 2008).

An overlay of beech chromatograms obtained at 300-700°C is shown in Figure 3.9. Event at temperature between 300-350°C indicates that holocellulose derived products with low molecular fractions (such as acetic acid) are poorly resolved at low temperatures probably due to poor purity unlike lignin derived products. The decomposition event at 350°C is only slightly different from 300°C, in that more low molecular products such as hydroxyacetaldehyde, acetol and acetic acid are produced. The decomposition of hexoses and pentoses produces acetic acid, 3-hydroxy-5, 6-dihydro-(4H)-pyran-4-one, dihydro-4-hydroxy-2(3H)-furanone, 2-furaldehyde, 2-hydroxy-2-cyclopentene-1-one, lactone derivatives, levoglucosan and a number of products suspected to be anhydrosugars. These peaks are suggested to be anhydrosugars because of the similarity between their fragmentation ions and that of levoglucosan. The temperature at this stage is not sufficient to induce severe radical fragmentation of the macromolecule. It is therefore expected that the formation of anhydrosugar from cellulose and hemicellulose will predominate, since favoured reactions are depolymerisation of the polysaccharides and dehydration of the resulting products.

Other major products detected at these low temperatures (300-350°C) are lignin derived products such as 4-vinyl syringol, sinapaldehyde, trans isoeugenol, 4-vinyl guaiacol, coniferyl alcohol. The relative amounts of these products vary among samples. For instance in spruce, the production of 2-hydroxymethyl-5-hydroxy-2,3-dihydro -(4H)-pyran-4-one ranked next to two anhydrosugars in concentration instead of 3-hydroxy-5,6-dihydro-(4H)-pyran-4-one found in beech. 2-hydroxymethyl-5-hydroxy-2,3-dihydro -(4H)-pyran-4-one is partially hydrogenated form of kojic acid, which has found application in food and cosmetic industries (to preserve or add colour).

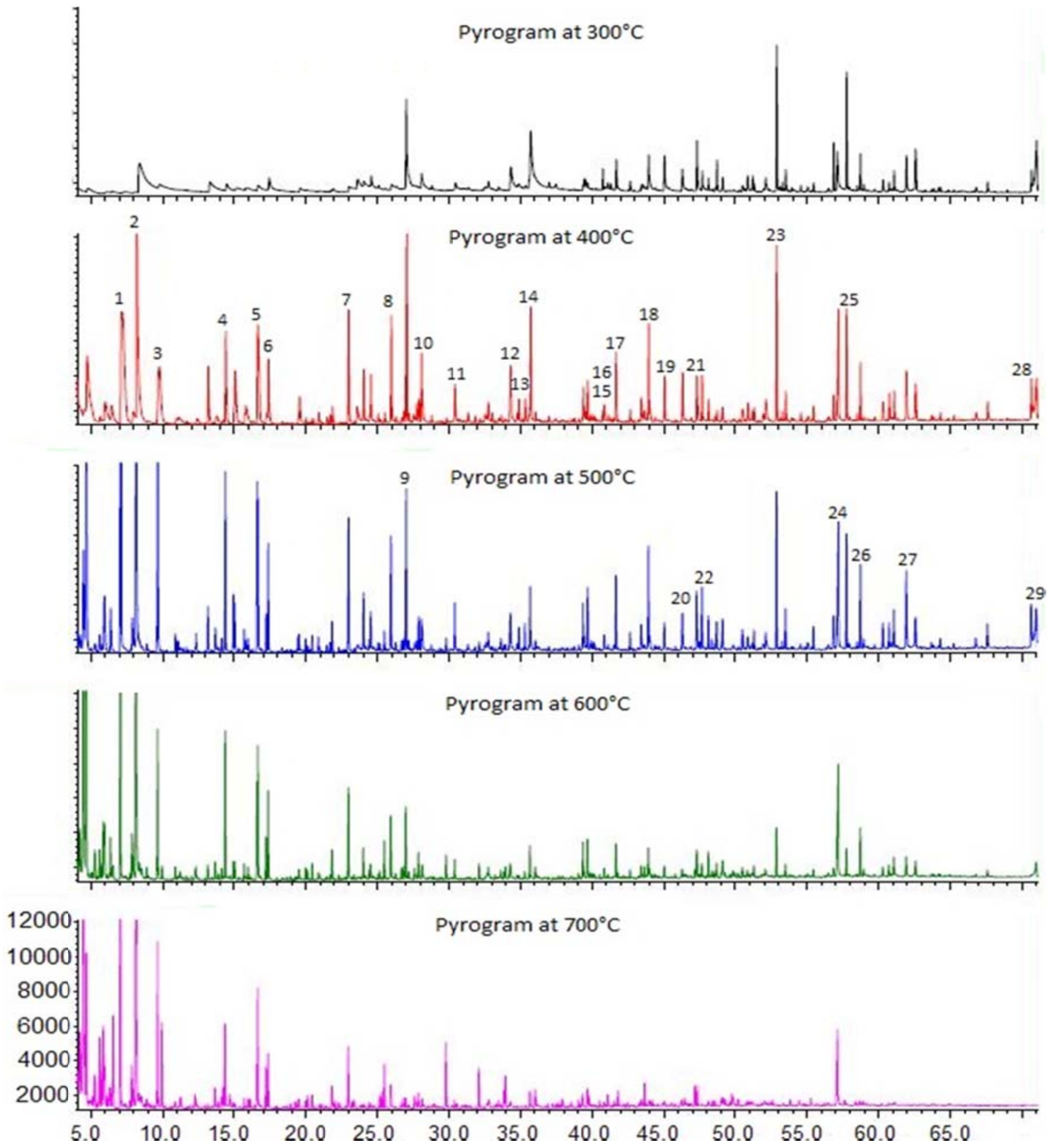


Figure 3.9: Beech chromatograms at 300, 400, 500, 600 and 700°C.

List: **1** *Acetaldehyde, hydroxy-;* **2** *Acetic acid;* **3** *Acetol (Hydroxypropanone);* **4** *Propionaldehyde, 3-hydroxy;* **5** *Oxopropanoic acid methylester;* **6** *Furaldehyde, 2-;* **7** *Cyclopentene-1-one, 2-hydroxy-2-;* **8** *Furanone, 2(5H)-;* **9** *Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-;* **10** *Pyran-2-one, 3,4-dihydro-6-methyl-2H-;* **11** *Guaiacol;* **12** *(S)-(+)-2',3'-Dideoxyribonolactone;* **13** *Guaiacol, 4-methyl;* **14** *Unknown anhydrosugar;* **15** *Dianhydro-mannopyranose, 1,4:3,6-;* **16** *Anhydro-ß-D-xylofuranose, 1,5-;* **17** *Guaiacol, 4-vinyl-;* **18** *Syringol;* **19** *2(3H)-Furanone, dihydro-4-hydroxy-;* **20** *Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-;* **21** *trans isoeugenol;* **22** *Syringol, 4-methyl;* **23** *Syringol, 4-vinyl;* **24** *Anhydro-ß-D-glucopyranose (Levoglucosan);* **25** *Syringol, 4-(1-Propenyl)- trans;* **26** *Syringaldehyde;* **27** *Coniferyl alcohol (trans);* **28** *Sinapyl alcohol (trans):* **29** *Sinapaldehyde (trans)*

Similar to beech, a list of products in all samples within these temperatures is dominated by anhydrosugars as result of the predominance of dehydration reaction. A summarised results of products identified in all samples is shown in Appendix 2A-E. Due to uncertainty of their peaks purity, results of volatiles at 300°C are not reported in the appendix.

The amount of non-aromatic aldehyde surged at 400°C across all samples, largely due to increase in the production of hydroxyacetaldehyde and 2-oxopropanal (methylglyoxal). Hydroxyacetaldehyde otherwise known as glycolaldehyde is the smallest possible molecule with both hydroxyl and aldehyde functional groups. Both chemical products can be formed as fragmentation products from holocellulose. LOMAX et al. (1991) however noted the possibility of their formation via reverse aldolisation process. The concentration of both products decay along the temperature range in most samples indicating that their production is in no way enhanced by the temperature changes.

Likewise, acetic acid, acetols, and 3-hydroxypropionaldehyde are amongst major pyrolysis products found in BCOs of the various samples. The concentration of both acetol and 3-hydroxypropionaldehyde remained fairly constant over a wide temperature range (400-600°C). Acetic acid in all samples (apart from spruce) maintains the highest concentration as individual chemical product, even after the loss of around one-fifth of its maximum concentration (attained at 400°C) at 700°C.

Variation in amounts of other important holocellulose derived chemical products such as levoglucosan, 3-hydroxy-5,6-dihydro-(4H)-pyran-4-one, furfural, 2(5H)-furanone, 2-hydroxy-2-cyclopentene-1-one is depicted in Figure 3.10 for four of the samples. Amounts of these products in both albizia and iroko largely correspond. Based on the direct proportionality between these products and pyrolysis temperatures, it can be suggested that they are directly obtained from various sugar units. In addition, their relative abundance at low temperatures (300-350°C), where severe fragmentation and possibility of fragments recombination is remote, further buttresses this assertion.

The transglycosylation process through which levoglucosan is formed (from cellulose) attained optimum condition at 500°C in almost all samples. And high amount of this anhydrosugar derivable from the angiosperm sample is further illustrated in Figure 3.10. This phenomenon probably suggests the easy of depolymerising cellulose from softwood compared to hardwood. Difference in structural composition of macromolecules (cellulose, hemicellulose and lignin) in various lignocellulose types could have influenced this disparity.

Virtually all lignin derived chemical products such as trans 4-(1-propenyl) syringol, trans coniferyl alcohol, syringol, guaiacol, trans 4-(1-propenyl) guaiacol, guaiacol, vanillin, syringyl acetone, 4-vinylsyringol, 4-vinylguaiacol and many more (too numerous to mention) attain their maximum yield at 500°C. They rapidly decreased from 550°C to almost insignificant fractions at 700°C, producing several smaller aromatic structures. An increment in concentrations of products, such as phenol, 4-ethyl phenol, *ortho*- and *meta*-cresol, hydroquinone and other related compounds is a pointer to this assertion.

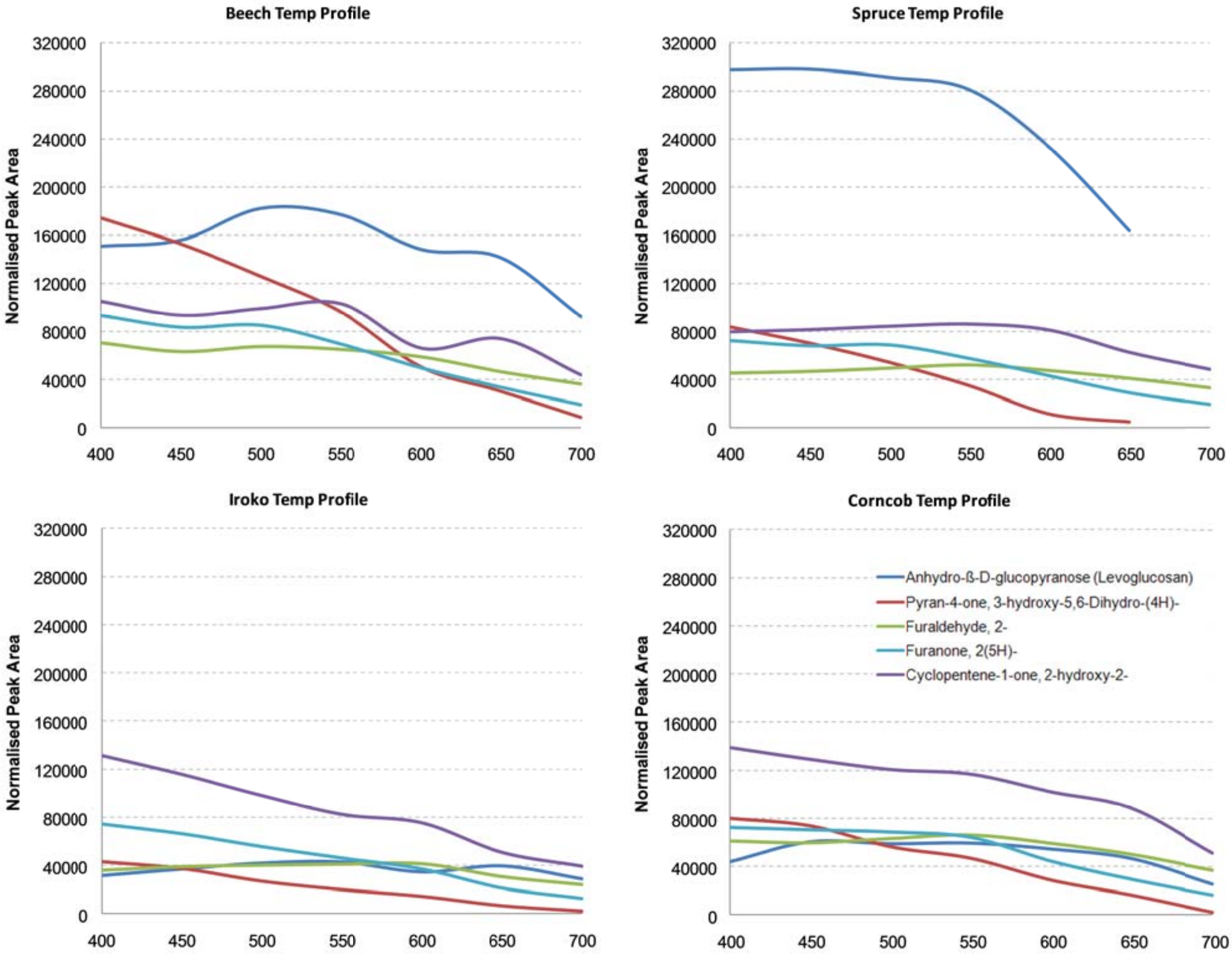


Figure 3.10: Trend in the variation of some holocellulose derived pyrolysis products along different pyrolysis temperature.

Vinyls of syringol and guaiacol are the most significant products as mentioned earlier. Because of their reactivity, these vinyls are found in lower concentration in BCOs compared to the pyrolysate from the analytical system. 4-vinyl phenol is the most abundant individual chemical product in corncob. Its concentration appears fairly unchanged across all temperatures up to 650°C as shown in Appendix 2E. The reason for the detection of vinyl phenol at high temperature even in other samples remains unclear beside their formation from secondary reaction between aromatic residue of lignin and other alkyl radicals.

3.2.3 Sample pre-treatment and impregnation

Pretreatment of lignocellulose by way of removing indigenous alkali and alkaline earth metals is a method that have been widely used to control the catalytic effects of these metals during pyrolysis (KLEEN and GELLERSTEDT, 1995). Large fractions of these metals are weakly bounded to lignocellulose on the surface. This enables their removal using water or more effectively, acidic solutions.

To understand the influence of metal contents on the pyrolysate compositions from various samples, feedstocks were washed with deionised water and 0.1M HCl. These media have been adjudged effective in the removal of exchangeable metal ions in lignocellulosic samples (KELLY et al., 1991; KLEEN and GELLERSTEDT, 1995; SCOTT et al., 2001). In addition, in order to understand the effects of individual monovalent and divalent ions, another set of water-washed samples were impregnated with NaCl and $CaCl_2$. A comprehensive description of the method is detailed in publication 2 (AZEEZ et al., 2011a). Results of major chemical components in pyrolysates obtained are discussed below.

3.2.3.1 Effects of washing and impregnation of beech

Summarised results of major chemical products obtained from the five lignocelluloses following pre-treatment and metal impregnation are shown in Appendices 3A-E. The comparison of effects of water and dilute acid washing indicates that the latter is more effective in the removal of metals attached to the biomass than the former. Both methods are however more effective on the European biomasses with low metal content than indigenous-metal-rich African samples. Of the two most abundant elements in all biomass, potassium is more readily removed than calcium. This effect is likely related to the forms in which the metals are attached in the biomass. This view has also been expressed by SCOTT et al. (2001). These metal ions have varying degree of influences on individual chemical component in lignocellulose pyrolysates, but their effects are much similar across all samples.

Based on tabulated results in Appendices 3A-E, the removal of metals from lignocellulose has more or less no effect on some holocellulose and lignin derived products and at the same time, enhancing or impeding the formation of other products. The removal of metals through washing with deionised water caused no significant effect on the amounts of acetic acid, propionaldeyhde, methylglyoxal, hydroxyacetaldehyde but unlike acid treated samples. As it can be seen in Figure 3.11, European samples washed with acid showed more significant reduction in the amount of hydroxyacetaldehyde than the African samples whereas in case of acetic acid, the reduction is almost negligible across all samples. Likewise, none of the added metals largely influenced the production of both products.

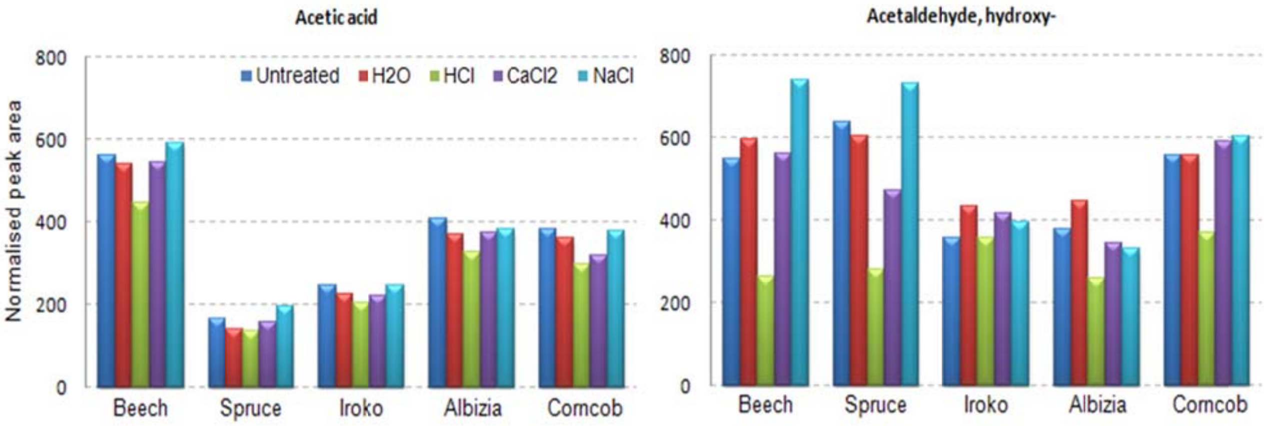


Figure 3.11: Effect of pre-treatments on the contents of acetic acid and hydroxyacetaldehyde.

A different scenario played out in case of holocellulose derived products such as 2(5H)-furanone, 2-hydroxy-2-cyclopentene-1-one, propanal and 3-pentanone. There is reduction in amounts of these species across all samples. As depicted in Figure 3.12, the effect is even more prominent in propanal and acetol, where less than one-third of the initial concentration is left in acid treated samples. It can be noted in sample dosed with monovalent and divalent metals that the former suppressed the production of these compounds while sodium enhanced their production. This observation is further buttressed by the degree of sodium ion enhancement in European samples, in which contents of the ion introduced was higher than initial concentration. Whereas in African biomasses, the amount of the indigenous ion removed through initial washing before the impregnation is more significant than the content introduced via impregnation. The observation on the action of monovalent sodium agrees with conclusions of previous investigators on catalytic effects of potassium on pyrolysis products (NOWAKOWSKI and JONES, 2008).

The most dramatic effect of the pretreatment is observed in important pyrolysis products such as furfural, 5-(hydroxymethyl)-2-furaldehyde, 2-hydroxymethyl-5-hydroxy-pyran-4-one, levoglucosan and other anhydrous sugars, found in large amount in corncob (Appendices 3A-E). These chemicals are decomposed cyclic-products from holocellulose, chiefly from cellulose. In comparison to products in which the removal of indigenous metal induces reduction, a reverse role is played by calcium in these cyclic-products, where the divalent calcium ion enhances their production but monovalent sodium suppresses.

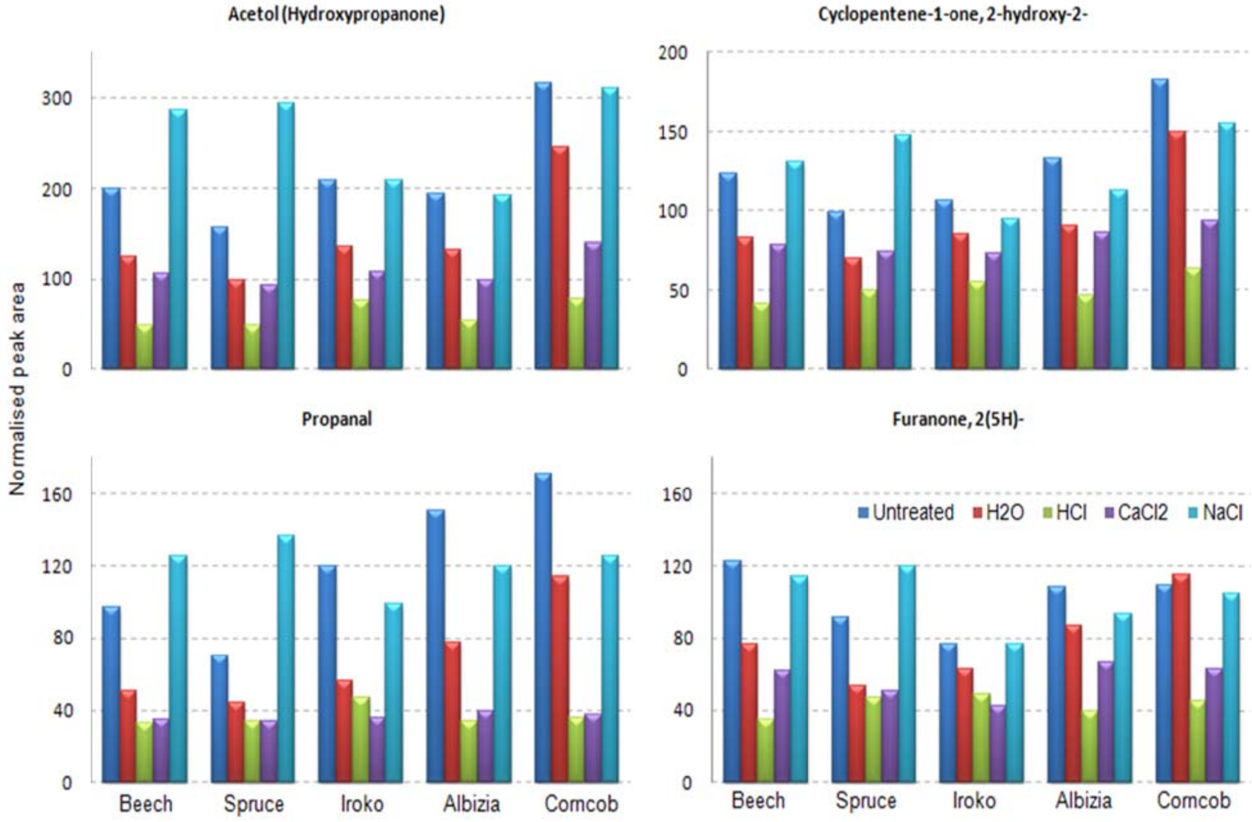


Figure 3.12: Effects of pretreatment on the contents of acetol, propanal, 2(5H)-furanone and 2-hydroxy-2-cyclopentene-1-one.

The distributions of some of these products in investigated samples are shown in Figure 3.13. It indicates that the amount of levoglucosan (in most cases) is about an order of 1 higher in acid treated samples compared to untreated samples. About half of this effect can be noted in the amount of 1, 5-anhydro-β-D-arabinofuranose (arabinosan) beside numerous peaks detected on samples chromatograms identified as unknown anhydrosugars. With increase in the formation of anhydrosugars and heavy pyrans, the average molecular weight (M_w) of the pyrolysate is expected to increase.

FAHMI et al. (2008) have observed that the removal of metal ions positively correlates with increased M_w. They made this assertion without any reference to the causative metal. Considering the effect of calcium ion addition on yields of these products, it can be suggested that the monovalent metals in lignocellulose especially potassium found in large amounts induce severe fragmentation of cellulose and probably hinder the formation of cellulose derived low molecular product via levoglucosan path as opined by SHAFIZADEH and his co-workers. This assertion is further sustained by the observation of low levoglucosan content in all untreated African samples (similar to the observation in their BCO), even though their glucose content largely compared with the contents in European biomasses.

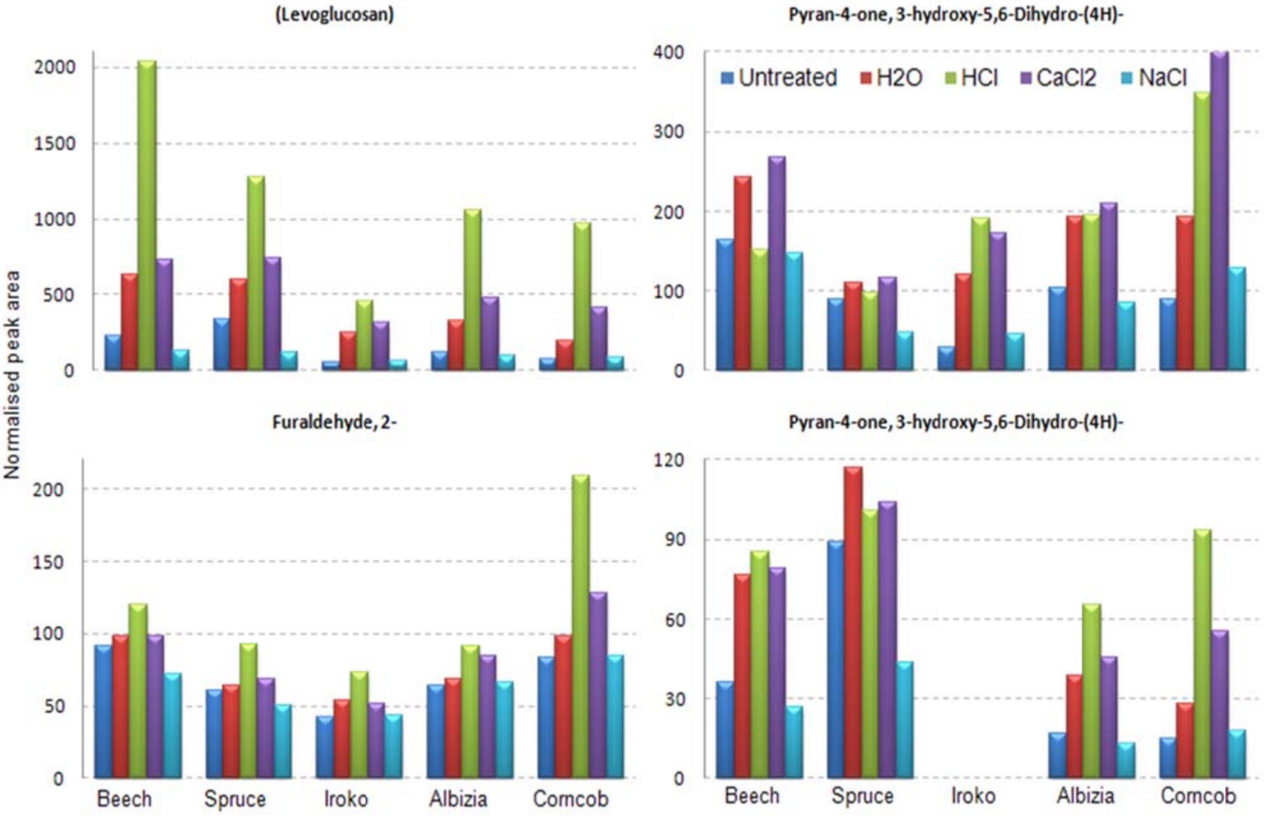


Figure 3.13: Effects of pre-treatments on some holocellulose derived cyclic-compounds.

Minor differences in yields of some of these products noted in European and African biomasses (Figure 3.13) are associated with the efficacy of removing metals in European biomasses compared to the African biomasses. A second glance at structures of many of these aforementioned cyclic-molecules shows that they are also formed from non-fragmented hexose sugar monomer, similar in manner levoglucosan is obtained from glucose in cellulose unit, except arabinosan, an aldopentose.

Many lignin derived products are less affected by the pre-treatment. However, prominent lignin products such as vinyls of guaiacol, syringol and phenol are somehow affected by the removal of ions, especially by the action of dilute acid. This effect is lesser in 4-vinyl guaiacol. In contrast to the event in sugar-derived cyclic-compounds, their yield is slightly enhanced in sodium-impregnated samples.

In conclusion, compositions of pyrolysis products produced at different temperatures illustrate differences in the pyrolysis products among the five samples. In general, holocellulose derived pyrolysis products dominate across the entire temperature range. In contrast to BCO from fluidised bed, 4-vinyls of guaiacol, syringol and phenol are noted to be most important individual chemical products derived from lignin across most samples. This observation may be related to the differences in the configuration of both pyrolysis systems. 4-vinyl guaiacol is an aromatic substance that has wide application as flavouring agent whereas 4-vinylphenol is a monomer that can be polymerised to obtain polystyrene-like plastic polymer known as poly-4-vinlyphenol (PVP).

The strategy of obtaining large fractions of individual chemical products via temperature variation may be seen as an unsuccessful approach. Maximum yields of most useful chemicals are obtainable at the optimum pyrolysis temperature (450-500°C). Although numerous aromatic products including various benzyl and phenyl based compounds are formed at higher temperature (600-700), their concentration in the resulting pyrolysate are very low and may prove uneconomical to separate. With appropriate and efficient separation techniques, the high yield of 4-vinylphenol obtainable from corncob make it a raw material of choose for the production of important monomers.

The removal of metals ion induced fragmentation patterns in lignocellulose different from the normal path thereby altering the concentration of various chemical components. An attractive means for the production of chemicals from lignocellulose via thermochemical conversion process may be attained by the removal of indigenous monovalent metal ions such as potassium and sodium. The subsequent introduction of divalent ion (calcium) will help to enhance the production of cyclic-compounds in high yield. This will reduce the amount of holocellulose derived low molecular chemical products that often complicate effective separation of main products. The high molecular fractions obtained can then be separated and individually converted to target (useful chemical) products.

3.3 Application of catalysts in the production of chemicals from lignocellulose (Publication 3)

The use of catalysts in thermochemical conversion of lignocelluloses is an option that have been discussed by many authors, as a means of obtaining useful chemical from renewable resources (BRIDGWATER, 1996; CARLSON et al., 2009; CARLSON et al., 2010). Most catalysts often employed are modified forms of different zeolites. In this study, five types of unmodified zeolites were employed to study their influence on individual pyrolysis product from lignocellulose. These catalysts include acidic zeolites, H-ZSM-5-80, H-ZSM-5-28, MSM-15, and basic zeolites, MSN-15 and SN-27. In order to limit the catalytic effects of indigenous metals, beech sample (which has low mineral contents) was adopted for the investigation. The samples were prepared as described by AZEEZ et al. (2011b) and pyrolysed using Py-GC/FID/MS. The evaluation of results was carried out using peak areas in FID signals.

3.3.1 Effects of catalysts

For the purpose of comparing yields of various pyrolysis products, FID peak areas of identified components in samples doped with catalyst were divided by corresponding peaks in untreated sample (US). The result of these ratios for various pyrolysis products is depicted in Appendix 4. The most affected products are the holocellulose derived pyrolysis products. The result indicates that the catalysts have specific effects mostly on volatile components derived from cellulose and hemicellulose. Even in cases of reduction in yields of some low molecular products, the extent of the reduction varies notwithstanding. This is illustrated by ratios of acetol, 3-butenal-one, 3-pentanone and 2-hydroxy-3-methyl cyclopentene-1-one. Samples treated with catalysts yield lower holocellulose derived products such as hydroxyacetaldehyde, acetic acid and 3-hydroxy propionaldehyde. These products are often found with prominent peaks in chromatograms (Py-GC/MS) of lignocelluloses. The extent of the reduction is minimal and negligible in some instances.

The specificity of the zeolites is less pronounced among lignin derived products such as guaiacol, 4-vinyl guaiacol, syringol and 4-vinyl syringol. Few exceptions to this observation might have been occasioned by secondary fragmentation of products such as sinapaldehyde into 4-methyl syringol. The secondary product can subsequently react with low molecular products from holocellulose to form indene compounds.

The PCA result for untreated and catalysed samples is depicted in Figure 3.14. It illustrates effects of the zeolites based on their activities. Approximately 75% of the validated variations in all the tested samples are described by PCs 1 and 2. Again, the categorisation in both PCs is predominantly influenced by carbohydrate derived volatile products as previously mentioned. The discrimination of MSM-15, HZSM-5-28 and HZSM-5-80 from the other two catalysts by PC1 explains about 50% of the variation occasioned by acidic property of the catalysts. This observation arises from improved yields of components such as 3-furaldehyde **(22)**, 3-hydroxy-5,6-dihydro-(4H)-pyran-4-one **(39)**, 4-methyl-syringol **(65)**, 6, hydroxyl-5, 7-dimethoxy-1H-indene (**75**), 6-hydroxy-7-methoxy-1H-indene **(68)**, and 1,6-anhydro-ß-D-glucopyranose **(76)** and anhydrosugar (**51**), among others. The delineation of the second PC is influenced by Si/Al, which enhances the production of chemical products such as 2-cyclopentene-1-,4-dione (**29**), 2,3-butandione **(3)**, 2-furaldehyde **(26)**, and indenes **(68, 69 and 75)**.

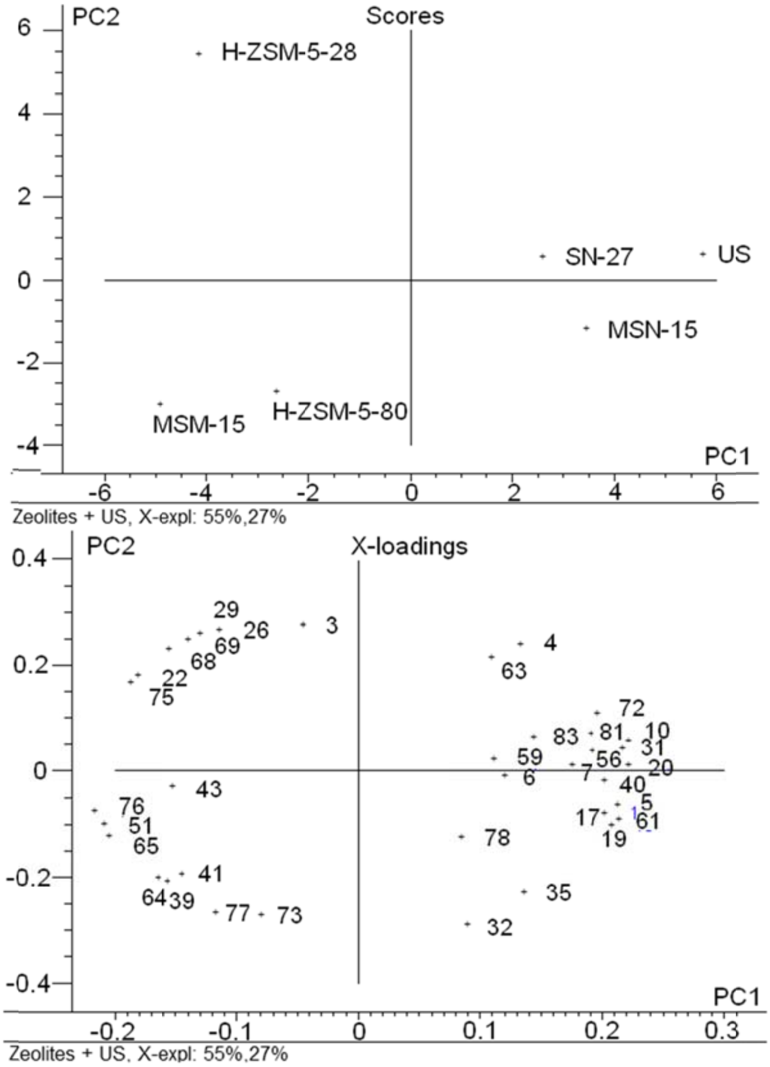


Figure 3.14: Score and loading plots for major pyrolysis products.

Both SN-27 and MSN-15 zeolites (with sodium active sites) have the least effect on beech sample but they enhance the yield of 2-butenal. The alkali metal suppresses the production of volatile products whose formation is via aldol-condensation reaction as seen in the ratio of anhydrosugars formed (Appendix 4). The monovalent ion inhibits the formation of levoglucosan and other anhydrosugars (Kleen and Gellerstedt, 1995; Richards and Shafizadeh, 1982).

Two causative reasons have been adduced by different authors to explain this effect. While Wang et al. (2006) suggested the lowering of pyrolysis temperature by basic catalysts as a possible reason, Choudhary and Srinivasan (1986) argued that the presence of sodium ions hinders diffusivity of high molecular products (anhydrosugar for example) due to reduction in the effective channel diameter.

It can be observed from Appendix 4 and Figure 3.15 that the most significant influence on the volatile product yield is induced by the acidic catalysts. Dominant organic products in this regard with marked effects are 1,6-anhydro-ß-D-glucopyranose (Levoglucosan), 1, 5-anhydro-ß-D-xylofuranose, furfural and an unknown carbohydrate. These products (especially levoglucosan and furfural) are important chemicals with wide industrial applications.

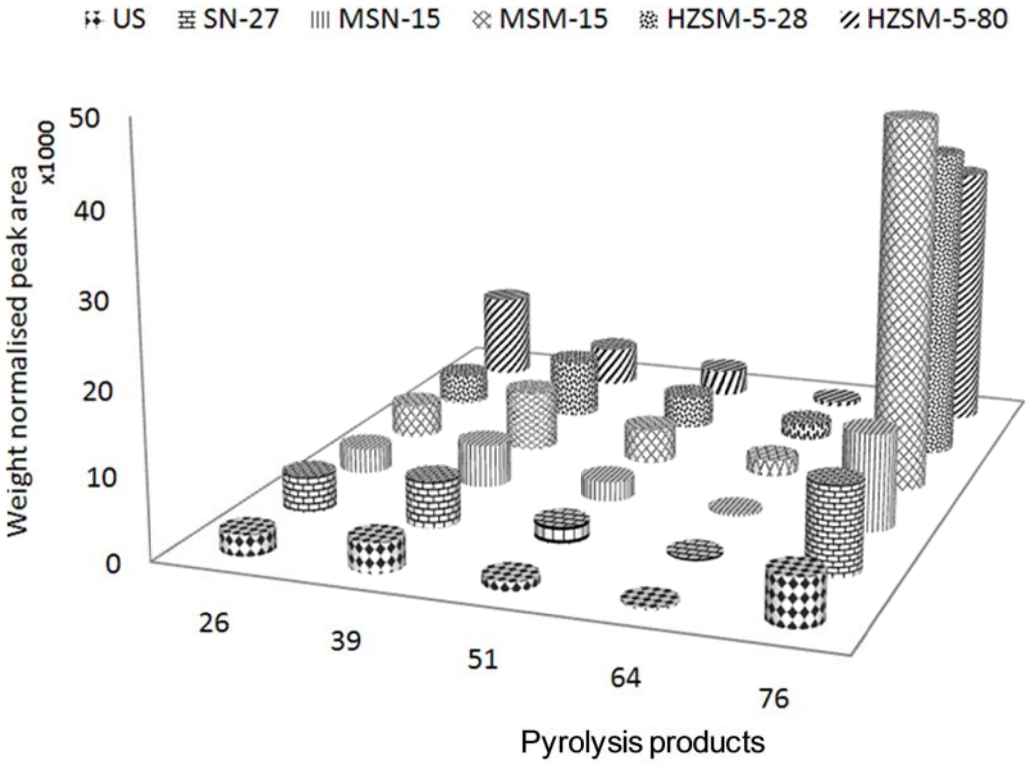


Figure 3.15: Distributions of some volatile products from beech holocellulose (components with annotated numbers are shown in Appendix 4).

All acidic catalysts promote the formation of levoglucosan. The greatest enhancement is induced by MSM-15 and HZSM-5-28 with about eight fold increment in samples dosed with 30% catalysts compared to the untreated sample. Peak area percentages of furfural and levoglucosan increased from 1.4% and 3.3% in untreated sample chromatograms to 4.6% and 20% in sample treated with HZSM-5-80 and MSM-15 (Figure 3.16a and b). Increased yield of furfural upon the application of zeolite catalyst to lignocelluloses have also been observed by ADAM et al. (2005). The observation on the yield of levoglucosan is exceptional if juxtaposed with reports by previous authors (ADAM et al., 2005; QIANG et al., 2009). The discrepancy could be related to the selectivity of different catalyst employed by these authors or methods of sample preparation.

Small pores of zeolite catalysts with varying characteristics accommodate active sites and often determine selectivity in reactions. CSICSERY (1984) explained that the selectivity arise from three forms namely reactant shape selectivity, product shape selectivity and transition state selectivity. Apart from this, there exist also externally active sites on zeolites' surface area and their pore mouth region. Chemical reactions on zeolites surface area limits reactivity through diffusion processes as a result of pore blockage (ZHENG et al., 2002). Therefore, the transformation of molecules by zeolites is not exclusively by diffusion.

All investigated zeolites exhibit selectivity in their enhancement of various decomposition products. The variation is even noted among H-ZSM-5 zeolites. Both H-ZSM-5 favour high yield of anhydrosugars (yield in H-ZSM-5-28 > H-ZSM-5). On the other hand, H-ZSM-5-80 selectively enhanced furfural yield as shown in Figure 3.16(b). The only difference between both catalysts lies in the silica-alumina ratio, which resulted in different acidic strengths.

The introduction of alumina into zeolites usually increases electronegativity, which is compensated by hydrogen in zeolite. Therefore, H-ZSM-5-28 with lower SiO_2/Al_2O_3 is more acidic than H-ZSM-5-80. Consequentially, the marked effect of the MSM-15 with respect to the highest amount of levoglucosan produced is related to its alumina content.

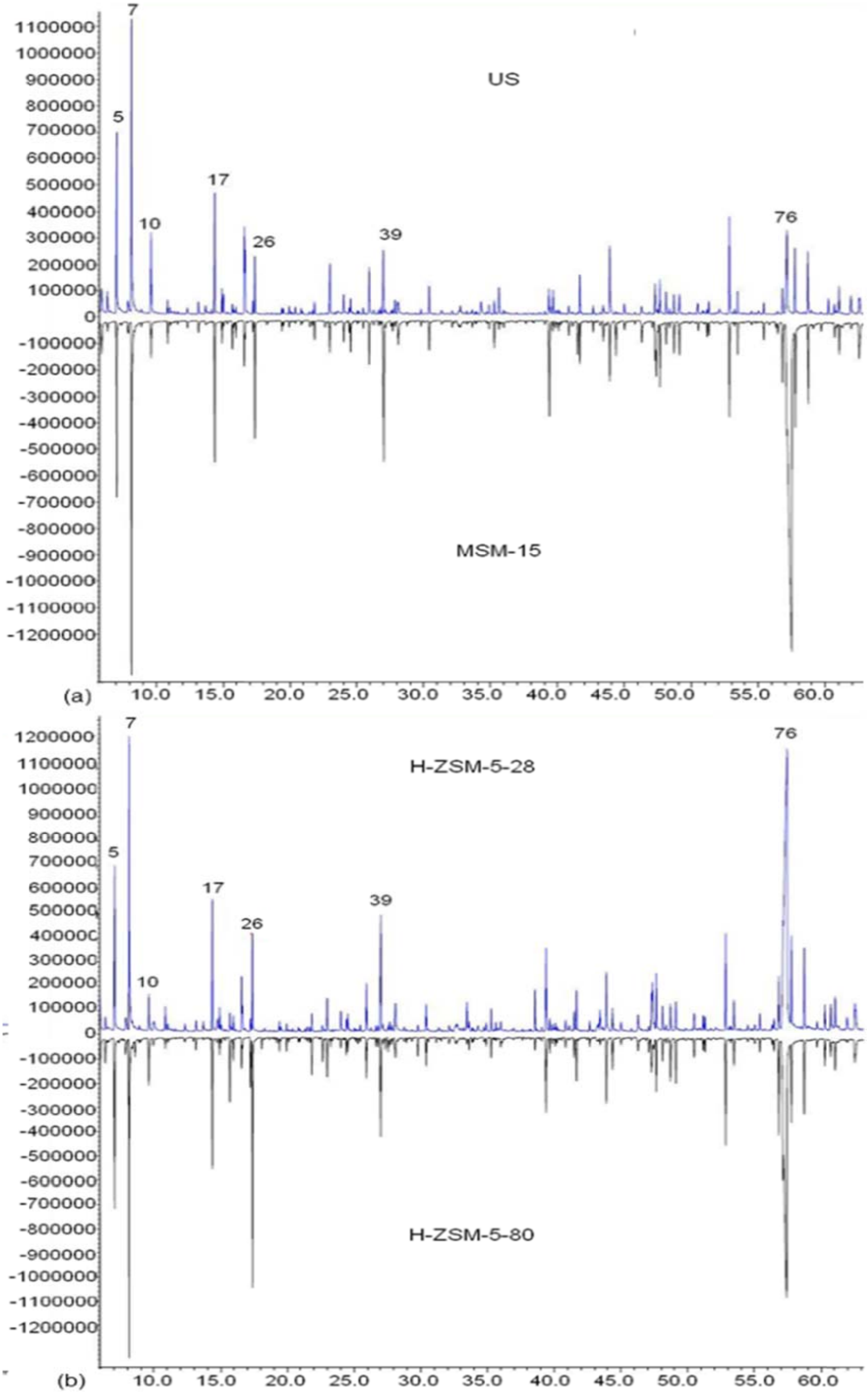


Figure 3.16: Overlay of TIC signals of (a) US vs. MSM-15 catalysed sample and (b) H-ZSM-5-28 vs. H-ZSM-5-80.

Silica-to-alumina ratio has been noted to enhance the role of Brönsted acidity in the activity of zeolite catalysts (WARD, 1970). Beside the strength of active sites, their location on zeolites catalyst is another factor that can influence their functionality. It has been observed that extra framework alumina (EFAL) promotes inductive effects with respect to Lewis acid sites present around the Brønsted acid sites. These two sites are the active sites that determine the reactivity of zeolites (NARBESHUBER et al., 1996). While the former is related to the EFAL, the latter is connected to aluminium located on zeolite frameworks.

On the sample preparation, it was observed in pre-trials of the various catalysts used without prior activation in furnace that the activities of various catalysts were negligible on the amount of levoglucosan and some other volatile products obtained. This phenomenon could have arisen due to the absorption of moisture on active sites of catalysts, thereby reducing the activity of the catalyst. The chromatogram of the sample with inactivated zeolite is identical with that of the untreated sample. In addition, the biomass sample was thoroughly mixed with the catalyst to form homogenous powder. There was a close interaction between the volatile product and surface area of the catalysts. This in effect, is expected to produce a different result when compared to a condition in which the catalyst was introduced as a thin bed above the sample as carried out by PATTIYA et al. (2008).

The role of acidity on the promotion of anhydrosugar formation during fast pyrolysis has been widely investigated (DOBELE et al., 2003; SHAFIZADEH et al., 1979). DOBELE et al. (2003) have noted that the cellulose glycosidic bonds undergo easy cleavage under the hydrolytic action of acid. And since the depolymerisation step preludes the formation of levoglucosan via transglycosylation, it could be deduced that the acidic zeolites act just like mineral acid by protonating the glycosidic oxygen. This results in the production of cellulose monomers, through which high yields of anhydrosugars are obtained. The suggested phenomenon can arise from the transfer of protons from Bronsted acid sites located outside zeolites pores as suggested by ZHENG et al. (2006).

In addition, it can be observed from the SEM images of untreated sample and sample treated with 10% MSM-15 (Figure 3.17) that chars formed after pyrolysis are significantly smaller in the latter. This morphological change is observed as a result of effective depolymerisation of the cellulose units. Although the yield of levoglucosan tripled when impregnated with 1%

phosphoric acid as reported by Dobele et al. (2003), results obtained under the action of MSM-15 and HZSM-5 acidic zeolites are outstanding.

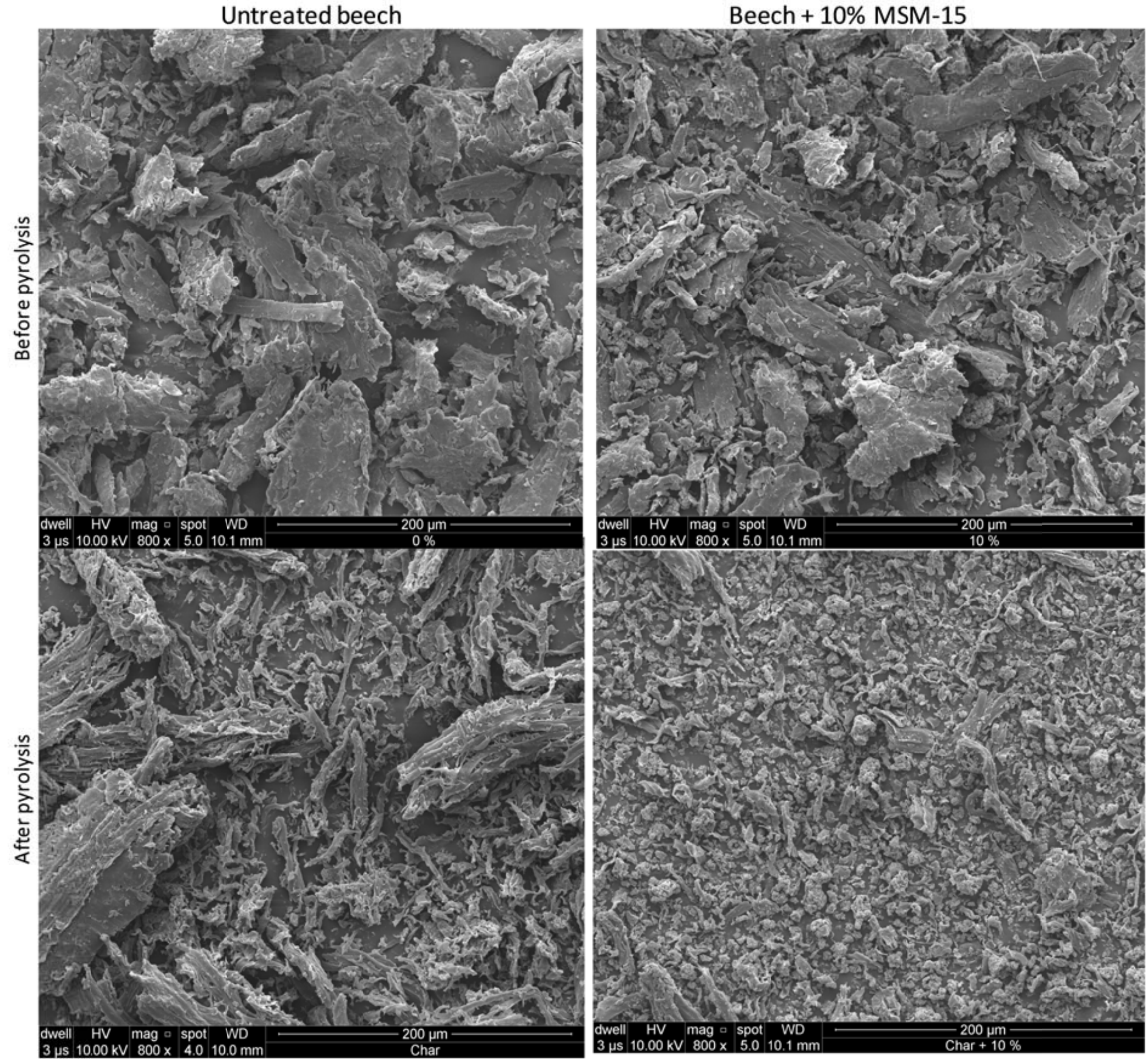


Figure 3.17: SEM result of catalysed and untreated beech before and after pyrolysis.

3.3.2 Effect of catalyst concentration

In order to evaluate the role of zeolite concentrations on the yield of major pyrolysis products, samples with gradient concentrations between 10% and 40% of MSM-15 and HZSM-5-80 on the basis of the biomass weight were prepared and duplicate pyrolysis were carried out for each sample. Yields of levoglucosan, furfural and some low volatiles responsible for the discrimination projected by PC2 were evaluated. According to the result obtained as shown in Figure 3.18, only levoglucosan and furfural yields are substantially influenced by different concentrations of MSM-15 and HZSM-5-80. A moderate increase in the amount of 6-hydroxy-5,7-dimethoxy-1H-indene is noticeable also in samples containing HZSM-5-80.

These observations further validate afore-discussed results. It also concurs with the findings of CARLSON et al. (2009), who observed that low feed-to-catalyst ratio improves products yield. Moreover, it buttresses previous assertion on the limited role of molecular diffusion through zeolites' pore when the reactivity of its surface area is high (ZHENG et al., 2002).

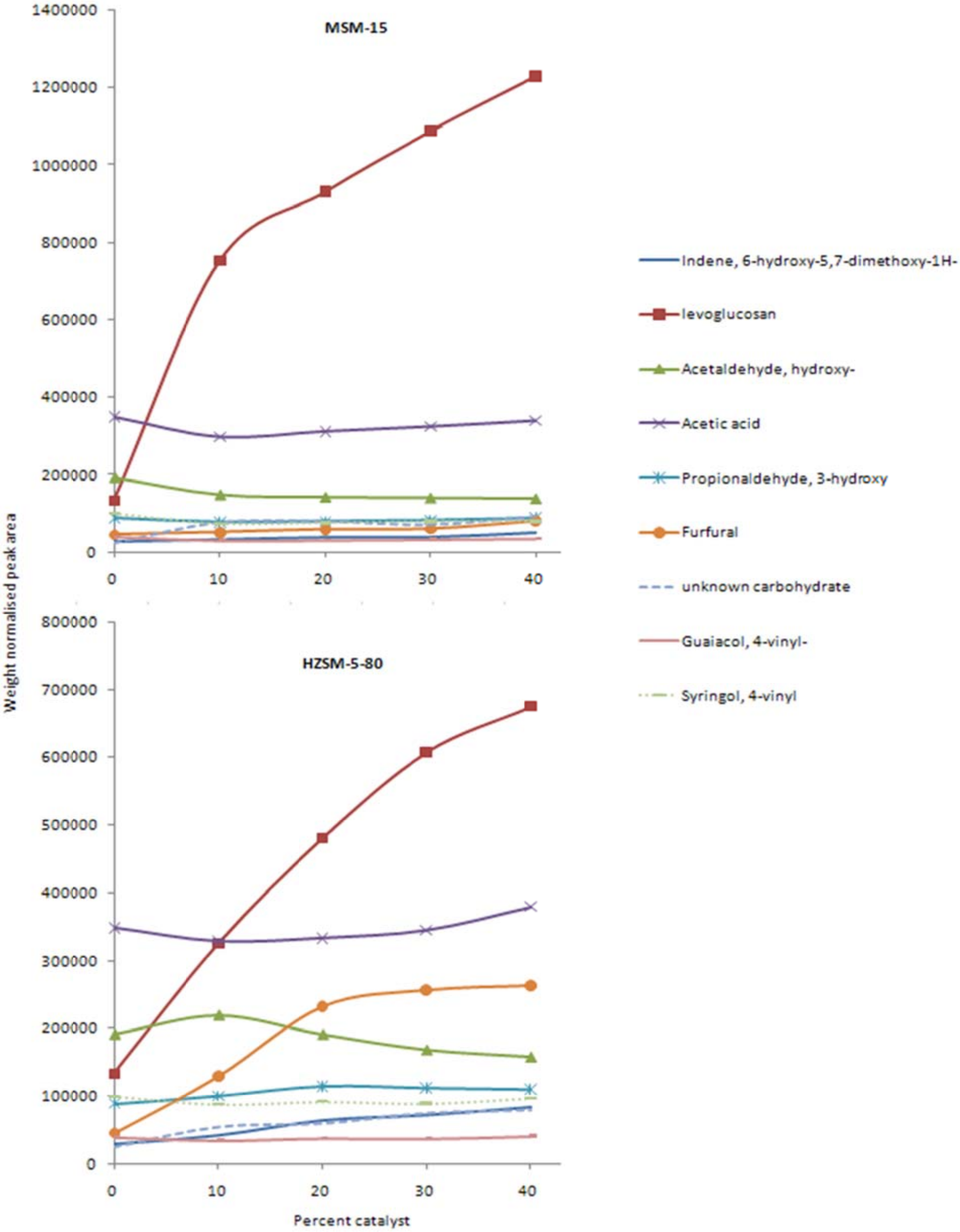


Figure 3.18: Effect of catalyst concentration on selected prominent volatile products

In conclusion, the use of catalysts to enhance high yields of important volatile products from lignocellulosic biomass is a practicable option towards achieving renewable chemical products. This may positively turn around the fortune of chemical industries that basically depend on petroleum as their raw materials. Zeolite is a catalyst of choice to attain this goal because they can be regenerated. Based on results obtained in this work, their action on the volatile products composition appeared to be highly selective depending on the method of sample preparation and the nature of the zeolites active sites. The acidic zeolites proved most influential on biomass pyrolysis volatile products.

High yields of levoglucosan obtained from the acidic zeolites possibly resulted from the predominance of dehydration process, following the depolymerisation by acidic zeolites. The amount of furfural is significantly enhanced by the catalyst with the highest silica-to-alumina ratio due to less activity at the surface area of the zeolite. Consequently, the contribution of the diffusion process in the modification of the thermochemical fragmentation products is enhanced. The method of sample preparation, which ensured close interaction between the catalyst and the sample, might have played a major role in the observed phenomenon.

3.4 Summary

In view of the daunting reality of the finite nature and more importantly, the environmental impacts of petroleum as major energy source, the necessity to source derive our energy needs from renewable sources has gained global acceptance. Chemical products for a variety of applications are but essential industrial raw materials that are almost exclusively obtained from petroleum at the moment. The conversion of lignocellulosic biomass offers promising renewable alternatives to obtain virtually all chemical products of important industrial applications ranging from low molecular chemical products to aromatic fractions from which benzene, toluene or xylene can be generated. Development of appropriate strategies for the conversion process is however required to harness this great potential. Thermochemical conversion of biomass (via fast pyrolysis) is one of the many conversion routes through which hundreds of chemical products such as acetic acid, levoglucosan, hydroxyacetaldehyde, furfural, 4-vinyl phenol, 4-vinly guaiacol etc. can be generated . Many of these products can be converted to obtain more useful or valuable chemical products.

Prior to conversion of different lignocellulosic wastes obtained from Africa and Europe, their physico-chemical analyses revealed differences in their chemical composition ranging from high extractive and mineral contents in lignocelluloses of Africa origin, aside from the general dissimilarities in major constituents (cellulose, hemicellulose and lignin) among different types of lignocellulose (hardwood, softwood and annual plants).

Thermochemical conversion of various lignocelluloses at 500°C in a fluidised bed reactor produced pyrolysate, char and mixture of non-condensable gases. The pyrolysate otherwise known as bio crude oil (BCO) contains over 85 chemical products, beside several other products (high molecular decomposition products), whose identities are difficult to ascertain. Individual concentrations of many of these products are very low in BCO, thereby complicating their separation process for identification.

Comparison of chemical products in BCOs from various lignocelluloses indicates that significant amounts of several products such as 4-vinyl phenol, 4-vinyl guaiacol and acetic acid are found mostly in corncob. The largest amount of levoglucosan, an anhydrosugar, was obtained in BCO of spruce. This is an indication that the composition of pyrolysis products in BCO is feedstock specific. Generally, the African biomasses yielded lesser pyrolysate owing to catalytic effects of high metal content present in the samples. The chemical compositions of BCOs from similar wood types (iroko, albizia and beech) largely correspond.

In order to improve the yield of individual chemical products in pyrolysates of different samples, parametric influence of pyrolysis temperature was employed. The result of this analysis carried out using an analytical pyrolysis unit shows that the possibility of efficiently producing volatile chemical products at temperature below the optimum value of 450-550°C is remote. It compromises the yield and the purity of individual chemical products. Conversions at temperatures above 600-700°C produced several benzyl and phenyl products mostly derived from lignocellulose lignin macromolecule. However, their concentrations are very low and may prove uneconomical to extract from several tens of products with higher fractions (mostly holocellulose derived products). Based on these observations, the best practice of fast pyrolysis at optimum temperature still stands as the best option to obtain high yields of chemical products.

The application of samples pretreatment such as water and dilute acid washing, to ameliorate the effect of indigenous mineral contents in feedstock on the pyrolysate yield, revealed that dilute acid washing is more effective than the former. Divalent ions were more easily removed than the monovalent ion, while larger fraction of these metals in both African hardwoods remains unaffected by any of the washing options. The removal of these ubiquitous minerals in feedstock alters the pyrolysis decomposition reaction pathway. The impregnation of calcium and sodium ions in water-washed samples shows that these alkali and alkaline earth metals are specific in their influences on the pyrolysate composition. While Ca^{2+} enhanced the formation of high molecular products from holocellulose, the presence of sodium slightly promoted formation of 4-vinyl phenol and 4-vinyl guaiacol from lignin macromolecule.

A careful manoeuvring of this pretreatment strategy may offer a novel approach for the production of chemicals from lignocellulose. For instance, it was noted that the impregnation of Ca^{2+} into lignocellulose promotes the cyclization of holocellulose-derived products leading to the substantial increase in cyclic compounds (up to order of 1 in some products especially levoglucosan). The production of compounds such as levoglucosan, furfural, 5-(hydroxymethyl)-2-furaldehyde, 2-hydroxymethyl-5-hydroxy-pyran-4-one at the expense of low molecular weight products will limit the number of chemical products in pyrolysate and facilitate separation processes. And specific cyclic compounds can then be carefully converted to more valuable chemical products.

The application of zeolite catalysts is another strategic option in modifying nature and yields of chemical products from thermochemical conversion of lignocellulose. Investigations using zeolite catalysts showed that the nature of the active site on zeolites and the alumina to silica ratio play most important roles, in addition to method of sample preparation. The use of acidic zeolites in a way similar to the operation in fluidized catalytic cracking (FCC) unit induced a very high concentration of levoglucosan and furfural owing to effective depolymerisation of the cellulose and hemicellulose unit occasioned by high cleavage of glycosidic bonds. The close interactions between sample particles and the zeolite surface area might have contributed to this dramatic effect via protonation.

By and large, the development of effective separation techniques, which is outside the focus of this research, is an essential operational tool required to obtain many of these products. Alternatively, in order to limit numbers of chemical components that make the separation of the complex mixture more difficult, depolymerisation of the macropolymers in lignocellulose to different fractions prior to thermochemical conversion is an option. The individual major fractions can be more effectively converted using optimum conditions and pretreatment to generate high yield of valuable chemical products.

Therefore, strategies to improve the use of BCO to obtain high value chemicals will involve choosing specific feedstocks for targeted chemical production based on original chemical composition, depolymerisation of the feedstocks to major constituent fractions, means of optimising specific chemicals by process modification through the use pretreatment options, and catalyst. Efficient fractionation and separation techniques must be developed to obtain various chemicals products in economical quantity.

4 Reference

ACIKGOZ, C., ONAY, O., KOCKAR, O.M., (2004): Fast pyrolysis of linseed: product yields and compositions. Journal of Analytical and Applied Pyrolysis 71, 417-429.

ADAM, J., BLAZSO, M., MESZAROS, E., STOCKER, M., NILSEN, M.H., BOUZGA, A., HUSTAD, J.E., GRONLI, M., OYE, G., (2005): Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts. Fuel 84, 1494-1502.

AGBLEVOR, F.A., BESLER, S., WISELOGEL, A.E., (1995): Fast pyrolysis of stored biomass feedstocks. Energy & Fuels 9, 635-640.

AGBLEVOR, F.A., DEUTCH, S.P., EHRMAN, C., RUIZ, R., (1997): An Overview of Development of Standard Analytical Procedures for Biomass Feedstocks. In: BRIDGWATER, A.V., BOOCOCK, D.G.B. (Eds.) Developments in thermochemical biomass conversion. Blackie Academic & Professional, London, pp. 723-730.

ALGER, M.S.M. (1997): Polymer Science Dictionary. (London, Chapman & Hall), p. 64.

ALVES, A., GIERLINGER, N., SCHWANNINGER, M., RODRIGUES, J., (2009): Analytical pyrolysis as a direct method to determine the lignin content in wood: Part 3. Evaluation of species-specific and tissue-specific differences in softwood lignin composition using principal component analysis. Journal of Analytical and Applied Pyrolysis 85, 30-37.

AMEN-CHEN, C., PAKDEL, H., ROY, C., (2001): Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresource Technology 79, 277-299.

ATES, F., ISIKDAG, M.A., (2008): Evaluation of the role of the pyrolysis temperature in straw biomass samples and characterization of the oils by GUMS. Energy & Fuels 22, 1936-1943.

AUTREY, S.T., ALNAJJAR, M.S., NELSON, D.A., FRANZ, J.A., (1991): Absolute rate constants for the .beta.-scission reaction of the 1-phenyl-2-phenoxypropyl radical: a model for radical reactions of lignin. The Journal of Organic Chemistry 56, 2197-2202.

AWAD, L., DEMANGE, R., ZHU, Y.-H., VOGEL, P., (2006): The use of levoglucosenone and isolevoglucosenone as templates for the construction of C-linked disaccharides. Carbohydrate Research 341, 1235-1252.

AZEEZ, A.M., MEIER, D., ODERMATT, J., WILLNER, T.(2011b): Effects of zeolites on volatile products of beech wood using analytical pyrolysis. Journal of Analytical and Applied Pyrolysis 91, 296-302.

AZEEZ, A.M., MEIER, D., ODERMATT, J., (2011a): Temperature dependence of fast pyrolysis volatile products from European and African biomasses. Journal of Analytical and Applied Pyrolysis 90, 81-92.

AZEEZ, A.M., MEIER, D., ODERMATT, J.R., WILLNER, T., (2010): Fast Pyrolysis of African and European Lignocellulosic Biomasses Using Py-GC/MS and Fluidized Bed Reactor. Energy & Fuels 24, 2078-2085.

BA, T., CHAALA, A., GARCIA-PEREZ, M., RODRIGUE, D., ROY, C., (2004): Colloidal Properties of Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark. Characterization of Water-Soluble and Water-Insoluble Fractions. Energy & Fuels 18, 704-712.

BAHNG, M.-K., MUKARAKATE, C., ROBICHAUD, D.J., NIMLOS, M.R., (2009): Current technologies for analysis of biomass thermochemical processing: A review. Analytica Chimica Acta 651, 117-138.

BALAT, M., (2008a): Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. Energy Sources Part a-Recovery Utilization and Environmental Effects 30, 620-635.

BALAT, M., (2008b): Mechanisms of thermochemical biomass conversion processes. Part 3: Reactions of liquefaction. Energy Sources Part a-Recovery Utilization and Environmental Effects 30, 649-659.

BAYERBACH, R., MEIER, D., (2009): Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin). Part IV: Structure elucidation of oligomeric molecules. Journal of Analytical and Applied Pyrolysis 85, 98-107.

BAYERBACH, R., NGUYEN, V.D., SCHURR, U., MEIER, D., (2006): Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) - Part III. Molar mass characteristics by SEC, MALDI-TOF-MS, LDI-TOF-MS, and Py-FIMS. Journal of Analytical and Applied Pyrolysis 77, 95-101.

BECH, N., JENSEN, P.A.D.-J., K., (2007): Ablative Flash Pyrolysis of Straw and Wood: Bench-Scale Results. In: 15th European Biomass Conference and Exhibition, Florence/Brussels.

BECIDAN, M., SKREIBERG, O., HUSTAD, J.E., (2007): Experimental study on pyrolysis of thermally thick biomass residues samples: Intra-sample temperature distribution and effect of sample weight ("scaling effect"). Fuel 86, 2754-2760.

BEHRENDT, F., NEUBAUER, Y., OEVERMANN, M., WILMES, B., ZOBEL, N., (2008): Direct liquefaction of biomass. Chemical Engineering & Technology 31, 667-677.

BINDER, J.B., RAINES, R.T., (2009): Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals. J Am Chem Soc 131, 1979-1985.

BOATENG, A.A., DAUGAARD, D.E., GOLDBERG, N.M., HICKS, K.B., (2007): Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production. Industrial & Engineering Chemistry Research 46, 1891-1897.

BOERJAN, W., RALPH, J., BAUCHER, M., (2003): Lignin Biosynthesis. Annu. Rev. Plant Biol. 54, 519-546.

BOON, J.J., (1992): Analytical pyrolysis mass-spectrometry - new vistas opened by temperature-resolved in-source PyMS. International Journal of Mass Spectrometry and Ion Processes 118/119, 755-787.

BOON, J.J., PASTOROVA, I., BOTTO, R.E., ARISZ, P.W., (1994): Structural Studies on Celulose Pyrolysis and Cellulose Chars by PyMS, FTIR, NMR and by Wet Chemical Techniques. Biomass and Bioenergy 7, 25-32.

BOUSTINGORRY, P., GROSSEAU, P., GUYONNET, R., GUILHOT, B., (2005): The influence of wood aqueous extractives on the hydration kinetics of plaster. Cement and Concrete Research 35, 2081-2086.

BOZELL, J.J., (2008): Feedstocks for the Future – Biorefinery Production of Chemicals from Renewable Carbon. CLEAN – Soil, Air, Water 36, 641-647.

BOZELL, J.J., HOLLADAY, J.E., JOHNSON, D., WHITE, J.F. (2007): Top Value-Added Chemicals from Biomass Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin. In: Biomass, BOZELL, J.J., HOLLADAY, J.E., JOHNSON, D., WHITE, J.F., eds. (Oak Ridge, TN, Pacific Northwest National Laboratory (PNNL); National Renewable Energy Laboratory (NREL), Office of Biomass Program (EERE)), pp. 1-66.

BRANCA, C., GIUDICIANNI, P., DI BLASI, C., (2003): GC/MS characterization of liquids generated from low-temperature pyrolysis of wood. Industrial & Engineering Chemistry Research 42, 3190-3202.

BREMER, J., (1991): Quantifizierung der Gerüstsubstanzen von Lignocellulosen durch analytische Pyrolyse-Gaschromatographie/Massenspektrometrie. PhD Dissertation. Universität Hamburg, Hamburg.

BRIDGWATER, A.V., (1996): Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. Catalysis Today 29, 285-295.

BRIDGWATER, A.V., (2010): Fast Pyrolysis of Biomass for Energy and Fuels. In: CROCKER, M. (Ed.) Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals. Royal Society of Chemistry, Cambridge, pp. 146-187.

BRIDGWATER, A.V., (2011): Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy In Press, Corrected Proof.

BRIDGWATER, A.V., PEACOCKE, G.V.C., (2000): Fast pyrolysis processes for biomass. Renew. Sust. Energ. Rev. 4, 1-73.

BRIENS, C., PISKORZ, J., BERRUTI, F. (2008): Biomass Valorization for Fuel and Chemicals Production -- A Review. (The Berkeley Electronic Press).

BUDGELL, D.R., HAYES, E.R., HELLEUR, R.J., (1987): Direct identification of pentoses and hexoses by pyrolysis/capillary gas chromatography. Analytica Chimica Acta 192, 243-253.

CARLSON, T., TOMPSETT, G., CONNER, W., HUBER, G., (2009): Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. Topics in Catalysis 52, 241-252.

CARLSON, T.R., JAE, J., LIN, Y.-C., TOMPSETT, G.A., HUBER, G.W., (2010): Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions. Journal of Catalysis 270, 110-124.

CHEN, G., ANDRIES, J., SPLIETHOFF, H., FANG, M., (2004): Biomass gasification integrated with pyrolysis in a circulating fluidised bed. Solar Energy 76, 345-349.

CHEN, G., ANDRIES, J., SPLIETHOFF, H., LEUNG, D.Y.C., (2003): Experimental investigation of biomass waste (rice straw, cotton stalk, and pine sawdust) pyrolysis characteristics. Energy Sources 25, 331-337.

CHERUBINI, F., (2010): The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management 51, 1412-1421.

CHERUBINI, F., JUNGMEIER, G., WELLISCH, M., WILLKE, T., SKIADAS, I., REE, R.V., JONG, E.D., (2009): Toward a common classification approach for biorefinery systems. Biofuels, Bioproducts and Biorefining 3, 534-546.

CHOUDHARY, V.R., SRINIVASAN, K.R., (1986): Sorption and diffusion of benzene in H-ZSM-5: Effect of Si/Al ratio, degree of cation exchange and pretreatment conditions. Journal of Catalysis 102, 328-337.

CLARK, J.H., (2007): Green chemistry for the second generation biorefinery—sustainable chemical manufacturing based on biomass. Journal of Chemical Technology & Biotechnology 82, 603-609.

CLARK, J.H., BUDARIN, V., DESWARTE, F.E.I., HARDY, J.J.E., KERTON, F.M., HUNT, A.J., LUQUE, R., MACQUARRIE, D.J., MILKOWSKI, K., RODRIGUEZ, A., SAMUEL, O., TAVENER, S.J., WHITE, R.J., WILSON, A.J., (2006): Green chemistry and the biorefinery: a partnership for a sustainable future. Green Chemistry 8, 853-860.

CONNER, A.H., NAGASAMPAGI, B.A., ROWE, J.W., (1980): Terpenoid and other extractives of western white pine bark. Phytochemistry 19, 1121-1131.

CSICSERY, S.M., (1984): Shape-selective catalysis in zeolites. Zeolites 4, 202-213.

CZERNIK, S., BRIDGWATER, A.V., (2004): Overview of applications of biomass fast pyrolysis oil. Energy & Fuels 18, 590-598.

DAI, X.W., WU, C.Z., LI, H.B., CHEN, Y., (2000): The fast pyrolysis of biomass in CFB reactor. Energy & Fuels 14, 552-557.

DAS, P., SREELATHA, T., GANESH, A., (2004): Bio oil from pyrolysis of cashew nut shell-characterisation and related properties. Biomass & Bioenergy 27, 265-275.

DAVIS, M.W., (1998): A Rapid Modified Method for Compositional Carbohydrate Analysis of Lignocellulosics by High pH Anion-Exchange Chromatography with Pulsed Amperometric Detection (HPAEC/PAD). J Wood Chem Technol 18, 235 - 252.

DAYTON, P.L.S.A.D.C. (2003): Preliminary Screening – Technical and Economic Assessment of Synthetsis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. (National Renewable Energy Laboratory).

DE RUITER, G.A., SCHOLS, H.A., VORAGEN, A.G.J., ROMBOUTS, F.M., (1992): Carbohydrate analysis of water-soluble uronic acid-containing polysaccharides with high-performance anion-exchange chromatography using methanolysis combined with TFA hydrolysis is superior to four other methods. Analytical Biochemistry 207, 176-185.

DE WILD, P.J., DEN UIL, H., REITH, J.H., KIEL, J.H.A., HEERES, H.J., (2009): Biomass valorisation by staged degasification A new pyrolysis-based thermochemical conversion option to produce value-added chemicals from lignocellulosic biomass. Journal of Analytical and Applied Pyrolysis 85, 124-133.

DEGUCHI, S., TSUJII, K., HORIKOSHI, K., (2006): Cooking cellulose in hot and compressed water. Chem Commun, 3293-3295.

DEMIRBAS, A., (2004): Current technologies for the thermo-conversion of biomass into fuels and chemicals. Energy Sources 26, 715-730.

DEMIRBAS, A., (2007a): Effect of temperature on pyrolysis products from biomass. Energy Sources Part a-Recovery Utilization and Environmental Effects 29, 329-336.

DEMIRBAS, A., (2007b): The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis. Fuel Processing Technology 88, 591-597.

DEMIRBAS, A., (2009): Political, economic and environmental impacts of biofuels: A review. Applied Energy 86, S108-S117.

DEMIRBAS, A., (2010): Biorefineries-For Biomass Upgrading Facilities. Springer-Verlag, London.

DEMIRBAS, A., ARIN, G., (2002): An overview of Biomass pyrolysis. Energy Sources 24, 471-482.

DEMIRBAS, A.H., SAHIN-DEMIRBAS, A., DEMIRBAS, A., (2004): Liquid fuels from agricultural residues via conventional pyrolysis. Energy Sources 26, 821-827.

DI BLASI, C., SIGNORELLI, G., DI RUSSO, C., REA, G., (1999): Product distribution from pyrolysis of wood and agricultural residues. Industrial & Engineering Chemistry Research 38, 2216-2224.

DIEBOLD, J.P., (1999): A Review of the Toxicity of Biomass Pyrolysis Liquids formed at Low Temepratures. In: BRIDGWATER, A.V. (Ed.) Fast Pyrolysis of Biomass: A Handbook. CPL Press, Newbury, UK, pp. 135-163.

DIEBOLD, J.P., (2002): A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-oils In: BRIDGWATER, A.V. (Ed.) Fast Pyrolysis of Biomass: A Handbook. CPL Press, Newsbury, UK, pp. 243-292.

DIONCO-ADETAYO, E.A., (2001): Utilization of wood wastes in Nigeria: a feasibility overview. Technovation 21, 55-60.

DOBELE, G., DIZHBITE, T., ROSSINSKAJA, G., TELYSHEVA, G., MIER, D., RADTKE, S., FAIX, O., (2003): Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis - A promising method for obtaining 1,6-anhydrosaccharides in high yields. Journal of Analytical and Applied Pyrolysis 68-9, 197-211.

DOBELE, G., ROSSINSKAJA, G., DIAZBITE, T., TELYSHEVA, G., MEIER, D., FAIX, O., (2005): Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. Journal of Analytical and Applied Pyrolysis 74, 401-405.

ELLIOTT, D.C., (2007): Historical developments in hydroprocessing bio-oils. Energy & Fuels 21, 1792-1815.

FAHMI, R., BRIDGWATER, A., DONNISON, I., YATES, N., JONES, J.M., (2008): The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. Fuel 87, 1230-1240.

FAIX, O. (2004a): Fundamentals of Wood Chemistry: IIB Accessory Components and Repeatition. (Hamburg, Wood Chemistry Technology, University of Hamburg), pp. 1-354.

FAIX, O. (2004b): Fundamentals of Wood Chemistry: Introduction, wood as a chemical raw material. (Hamburg, Wood Chemistry Technology, University of Hamburg), pp. 1-515.

FENGEL, D., WEGENER, G., (1984): Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter & Co., Berlin, 26-60 pp.

FRENCH, R., CZERNIK, S., (2010): Catalytic pyrolysis of biomass for biofuels production. Fuel Processing Technology 91, 25-32.

GALLETTI, G.C., REEVES, J.B., BOCCHINI, P., (1997): Analytical pyrolysis as a tool to determine chemical changes in maize stovers during growth. Journal of Analytical and Applied Pyrolysis 39, 105-114.

GARCIA-PEREZ, M., ADAMS, T.T., GOODRUM, J.W., GELLER, D.P., DAS, K.C., (2007): Production and fuel properties of pine chip Bio-oil/Biodiesel blends. Energy & Fuels 21, 2363-2372.

GARCIA-PEREZ, M., WANG, S., SHEN, J., RHODES, M., LEE, W.J., LI, C.Z., (2008a): Effects of temperature on the formation of lignin-derived oligomers during the fast pyrolysis of Mallee woody biomass. Energy & Fuels 22, 2022-2032.

GARCIA-PEREZ, M., WANG, X.S., SHEN, J., RHODES, M.J., TIAN, F.J., LEE, W.J., WU, H.W., LI, C.Z., (2008b): Fast pyrolysis of oil mallee woody biomass: Effect of temperature on the yield and quality of pyrolysis products. Industrial & Engineering Chemistry Research 47, 1846-1854.

GÍRIO, F.M., FONSECA, C., CARVALHEIRO, F., DUARTE, L.C., MARQUES, S., BOGEL-LUKASIK, R., (2010): Hemicelluloses for fuel ethanol: A review. Bioresource Technology 101, 4775-4800.

GRAY, K.A., ZHAO, L., EMPTAGE, M., (2006): Bioethanol. Current Opinion in Chemical Biology 10, 141-146.

HALL, D.O., SCRASE, J.I., (2005): Biomass energy in sub-Saharan Africa. In: LOW, P.S. (Ed.) Climate Change and Africa. Cambridge University Press, New York, pp. 107-112.

HORNE, P.A., WILLIAMS, P.T., (1995): The effect of zeolite ZSM-5 catalyst deactivation during the upgrading of biomass-derived pyrolysis vapors. Journal of Analytical and Applied Pyrolysis 34, 65-85.

INGRAM, L., MOHAN, D., BRICKA, M., STEELE, P., STROBEL, D., CROCKER, D., MITCHELL, B., MOHAMMAD, J., CANTRELL, K., PITTMAN, C.U., (2008): Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils. Energy & Fuels 22, 614-625.

IOANNIDOU, O., ZABANIOTOU, A., ANTONAKOU, E.V., PAPAZISI, K.M., LAPPAS, A.A., ATHANASSIOU, C., (2009): Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations. Renew. Sust. Energ. Rev. 13, 750-762.

JARVIS, M.W., HAAS, T.J., DONOHOE, B.S., DAILY, J.W., GASTON, K.R., FREDERICK, W.J., NIMLOS, M.R., (2010): Elucidation of Biomass Pyrolysis Products Using a Laminar Entrained Flow Reactor and Char Particle Imaging. Energy & Fuels, 324-336.

JEKAYINFA, S.O., SCHOLZ, V., (2009): Potential Availability of Energetically Usable Crop Residues in Nigeria. Energy Sources Part A-Recovery Util. Environ. Eff. 31, 687-697.

KAAR, W.E., COOL, L.G., MERRIMAN, M.M., BRINK, D.L., (1991): The Complete Analysis of Wood Polysaccharides Using HPLC. J Wood Chem Technol 11, 447 - 463.

KELLY, J., MACKEY, M., HELLEUR, R.J., (1991): Quantitative analysis of saccharides in wood pulps by quartz-tube pulse pyrolysis--polar phase gas chromatography. Journal of Analytical and Applied Pyrolysis 19, 105-117.

KEOWN, D.M., HAYASHI, J.I., LI, C.Z., (2008): Effects of volatile-char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass. Fuel 87, 1187-1194.

KINOSHITA, C.M., TURN, S.Q., (2003): Production of hydrogen from bio-oil using CaO as a CO2 sorbent. International Journal of Hydrogen Energy 28, 1065-1071.

KLAP, V.A., BOON, J.J., HEMMINGA, M.A., VAN SOELEN, J., (1998): Chemical characterization of lignin preparations of fresh and decomposing Spartina anglica by pyrolysis mass spectrometry. Organic Geochemistry 28, 707-727.

KLEEN, M., GELLERSTEDT, G., (1995): Influence of inorganic species on the formation of polysaccharide and lignin degradation products in the analytical pyrolysis of pulps. Journal of Analytical and Applied Pyrolysis 35, 15-41.

KLEINERT, M., BARTH, T., (2008): Phenols from lignin. Chemical Engineering & Technology 31, 736-745.

KLEMM, D., HEUBLEIN, B., FINK, H.-P., BOHN, A., (2005): Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angewandte Chemie International Edition 44, 3358-3393.

KUCUK, M.M., DEMIRBAS, A., (1997): Biomass conversion processes. Energy Conversion and Management 38, 151-165.

LEDE, J., (2003): Comparison of contact and radiant ablative pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis 70, 601-618.

LEIBOLD, H., HORNUNG, A., SEIFERT, H., (2008): HTHP syngas cleaning concept of two stage biomass gasification for FT synthesis. Powder Technology 180, 265-270.

LI, J., KISARA, K., DANIELSSON, S., LINDSTRÖM, M.E., GELLERSTEDT, G., (2007): An improved methodology for the quantification of uronic acid units in xylans and other polysaccharides. Carbohydrate Research 342, 1442-1449.

LICHTENTHALER, F.W., (2002): Unsaturated O- and N-Heterocycles from Carbohydrate Feedstocks. Accounts of Chemical Research 35, 728-737.

LIN, L.L., YAN, R., LIU, Y.Q., JIANG, W.J., (2010): In-depth investigation of enzymatic hydrolysis of biomass wastes based on three major components: Cellulose, hemicellulose and lignin. Bioresource Technology 101, 8217-8223.

LIU, Q., WANG, S.R., WANG, K.G., GUO, X.J., LUO, Z.Y., CEN, K.F., (2008): Mechanism of Formation and Consequent Evolution of Active Cellulose during Cellulose Pyrolysis. Acta Physico-Chimica Sinica 24, 1957-1963.

LOMAX, J.A., COMMANDEUR, J.M., ARISZ, P.W., BOON, J.J., (1991): Characterisation of oligomers and sugar ring-cleavage products in the pyrolysate of cellulose. Journal of Analytical and Applied Pyrolysis 19, 65-79.

LUO, Z.Y., WANG, S., LIAO, Y.F., ZHOU, J.S., GU, Y.L., CEN, K.F., (2004): Research on biomass fast pyrolysis for liquid fuel. Biomass & Bioenergy 26, 455-462.

LV, D., XU, M., LIU, X., ZHAN, Z., LI, Z., YAO, H., (2010): Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. Fuel Processing Technology 91, 903-909.

MAJERSKI, P., PISKORZ, J., RADLEIN, D., (2006): Production of glycolaldehyde by hydrous thermolysis of sugars. PATENT, U.S. 1-12

MASCHIO, G., LUCCHESI, A., STOPPATO, G., (1994): Production of syngas from biomass. Bioresource Technology 48, 119-126.

MATHEWS, J.F., TEPYLO, M.G., EAGER, R.L., PEPPER, J.M., (1985): Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst. The Canadian Journal of Chemical Engineering 63, 686-689.

MEIER, D., BRIDGWATER, A.V., DI BLASI, C., PRINS, W., (1997): Integrated chemicals and fuels recovery from pyrolysis liquids generated by ablative pyrolysis. M. Kaltschmitt and A.V. Bridgwater, 516-527 pp.

MEIER, D., FAIX, O., (1999): State of the art of applied fast pyrolysis of lignocellulosic materials - a review. Bioresource Technology 68, 71-77.

MOHAN, D., PITTMAN, C.U., STEELE, P.H., (2006): Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels 20, 848-889.

MULLEN, C.A., BOATENG, A.A., HICKS, K.B., GOLDBERG, N.M., MOREAU, R.A., (2009a): Analysis and Comparison of Bio-Oil Produced by Fast Pyrolysis from Three Barley Biomass/Byproduct Streams. Energy & Fuels 24, 699–706.

MULLEN, C.A., STRAHAN, G.D., BOATENG, A.A., (2009b): Characterization of Various Fast-Pyrolysis Bio-Oils by NMR Spectroscopy. Energy & Fuels 23, 2707-2718.

NARBESHUBER, T.F., BRAIT, A., SESHAN, K., LERCHER, J.A., (1996): The influence of extraframework aluminum on H-FAU catalyzed cracking of light alkanes. Applied Catalysis A: General 146, 119-129.

NAVARRO, M.V., MURILLO, R., MASTRAL, A.M., PUY, N., BARTROLI, J., (2009): Application of the Distributed Activation Energy Model to Biomass and Biomass Constituents Devolatilization. Aiche Journal 55, 2700-2715.

NOWAKOWSKI, D.J., JONES, J.M., (2008): Uncatalysed and potassium-catalysed pyrolysis of the cell-wall constituents of biomass and their model compounds. Journal of Analytical and Applied Pyrolysis 83, 12-25.

OASMAA, A., CZERNIK, S., (1999): Fuel Oil Quality of Biomass Pyrolysis OilsState of the Art for the End Users. Energy & Fuels 13, 914-921.

OASMAA, A., KUOPPALA, E., (2008): Solvent Fractionation Method with Brix for Rapid Characterization of Wood Fast Pyrolysis Liquids. Energy & Fuels 22, 4245-4248.

OASMAA, A., KUOPPALA, E., GUST, S., SOLANTAUSTA, Y., (2003a): Fast pyrolysis of forestry residue. 1. Effect of extractives on phase separation of pyrolysis liquids. Energy & Fuels 17, 1-12.

OASMAA, A., KUOPPALA, E., SOLANTAUSTA, Y., (2003b): Fast pyrolysis of forestry residue. 2. Physicochemical composition of product liquid. Energy & Fuels 17, 433-443.

OASMAA, A., MEIER, D., (2005): Norms and standards for fast pyrolysis liquids - 1. Round robin test. Journal of Analytical and Applied Pyrolysis 73, 323-334.

OASMAA, A., PEACOCKE, C. (2001): A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. FINLAND, T.R.C.O., ed. (Vuorimiehentie, Finland, VTT Publications), pp. 1-65.

OASMAA, A., SOLANTAUSTA, Y., ARPIAINEN, V., KUOPPALA, E., SIPILA, K., (2010): Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. Energy & Fuels 24, 1380-1388.

PAN, W.-P., RICHARDS, G.N., (1989): Influence of metal ions on volatile products of pyrolysis of wood. Journal of Analytical and Applied Pyrolysis 16, 117-126.

PARN, L., (2005): The production of wood-based bio-oil in Estonia. Transactions of the Faculty of Forestry, Estonian Agricultural University, 88-102.

PATTIYA, A., TITILOYE, J.O., BRIDGWATER, A.V., (2008): Fast pyrolysis of cassava rhizome in the presence of catalysts. Journal of Analytical and Applied Pyrolysis 81, 72-79.

PENG, F., BIAN, J., REN, J.-L., PENG, P., XU, F., SUN, R.-C., Fractionation and characterization of alkali-extracted hemicelluloses from peashrub. Biomass and Bioenergy In Press, Corrected Proof.

PENG, P., BIAN, J., SUN, R.-C., (2010): Extractives. In: Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels. Elsevier, Amsterdam, pp. 49-72.

PETROCELLI, F.P., KLEIN, M.T., (1984): Model reaction pathways in Kraft lignin pyrolysis. Macromolecules 17, 161-169.

PISKORZ, J., MAJERSKI, P., RADLEIN, D., VLADARS-USAS, A., SCOTT, D.S., (2000): Flash pyrolysis of cellulose for production of anhydro-oligomers. Journal of Analytical and Applied Pyrolysis 56, 145-166.

PISKORZ, J., RADLEIN, D., SCOTT, D.S., (1986): On the mechanism of the rapid pyrolysis of cellulose. Journal of Analytical and Applied Pyrolysis 9, 121-137.

PISKORZ, J., RADLEIN, D.S.A.G., SCOTT, D.S., CZERNIK, S., (1989): Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. Journal of Analytical and Applied Pyrolysis 16, 127-142.

PONDER, G.R., RICHARDS, G.N., (1993): Pyrolysis of some 13C-labeled glucans: a mechanistic study. Carbohydrate Research 244, 27-47.

POUWELS, A.D., EIJKEL, G.B., BOON, J.J., (1989): Curie-point pyrolysis-capillary gas chromatography-high-resolution mass spectrometry of microcrystalline cellulose. Journal of Analytical and Applied Pyrolysis 14, 237-280.

PU, Y.Q., ZHANG, D.C., SINGH, P.M., RAGAUSKAS, A.J., (2008): The new forestry biofuels sector. Biofuels Bioproducts & Biorefining-Biofpr 2, 58-73.

QIANG, L., WEN-ZHI, L., DONG, Z., XI-FENG, Z., (2009): Analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) of sawdust with Al/SBA-15 catalysts. Journal of Analytical and Applied Pyrolysis 84, 131-138.

RADLEIN, D., PISKORZ, J., SCOTT, D.S., (1991): Fast pyrolysis of natural polysaccharides as a potential industrial process. Journal of Analytical and Applied Pyrolysis 19, 41-63.

RAVEENDRAN, K., GANESH, A., KHILAR, K.C., (1995): Influence of mineral matter on biomass pyrolysis characteristics. Fuel 74, 1812-1822.

RAVEENDRAN, K., GANESH, A., KHILAR, K.C., (1996): Pyrolysis characteristics of biomass and biomass components. Fuel 75, 987-998.

RICHARDS, G.N., (1987): Glycolaldehyde from pyrolysis of cellulose. Journal of Analytical and Applied Pyrolysis 10, 251-255.

RICHARDS, G.N., SHAFIZADEH, F., (1982): Formation of "Glucometasaccharinolactones" in the pyrolysis of curdlan, A (1-->3)-[beta]--glucan. Carbohydrate Research 106, 83-91.

RICHARDS, G.N., ZHENG, G.C., (1991): Influence of metal-ions and of salts on products from pyrolysis of wood - Applications to thermochemical processing of newsprint and biomass. Journal of Analytical and Applied Pyrolysis 21, 133-146.

RODRÍGUEZ-REINOSO, F., MARTÍNEZ-ESCANDELL, M., TORREGROSA, P., MARSH, H., GÓMEZ DE SALAZAR, C., ROMERO-PALAZÓN, E., (2001): Pyrolysis of petroleum residues: III. Kinetics of pyrolysis. Carbon 39, 61-71.

ROMAN-LESHKOV, Y., BARRETT, C.J., LIU, Z.Y., DUMESIC, J.A., (2007): Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. Nature 447, 982-985.

ROWE, J.W., BOWER, C.L., WAGNER, E.R., (1969): Extractives of jack pine bark: Occurrence of cis- and trans-pinosylvin dimethyl ether and ferulic acid esters. Phytochemistry 8, 235-241.

SAIZ-JIMENEZ, C., DE LEEUW, J.W., (1986): Lignin pyrolysis products: Their structures and their significance as biomarkers. Organic Geochemistry 10, 869-876.

SAMBO, A.S. (2009): Strategic Developments In Renewable Energy In Nigeria. In: IAEE Energy Forum (International Association for Energy Economics), pp. 15-19.

SAMOLADA, M.C., STOICOS, T., VASALOS, I.A., (1990): An investigation of the factors controlling the pyrolysis product yield of greek wood biomass in a fluidized bed. Journal of Analytical and Applied Pyrolysis 18, 127-141.

SARKAR, S., KUMAR, A., (2010): Large-scale biohydrogen production from bio-oil. Bioresource Technology 101, 7350-7361.

SCHOLZE, B., HANSER, C., MEIER, D., (2001): Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) Part II. GPC, carbonyl goups, and 13C-NMR. Journal of Analytical and Applied Pyrolysis 58-59, 387-400.

SCHOLZE, B., MEIER, D., (2001): Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY–GC/MS, FTIR, and functional groups. Journal of Analytical and Applied Pyrolysis 60, 41-54.

SCOTT, D.S., PATERSON, L., PISKORZ, J., RADLEIN, D., (2001): Pretreatment of poplar wood for fast pyrolysis: rate of cation removal. Journal of Analytical and Applied Pyrolysis 57, 169-176.

SCOTT, D.S., PISKORZ, J., RADLEIN, D., MAJERSKI, P., (1995): Process for the production of anhydrosugars from lignin and cellulose containing biomass by pyrolysis. PATENT, U.S. 5,395,455, 1995.

SENSOZ, S., ANGIN, D., (2008): Pyrolysis of safflower (Charthamus tinctorius L.) seed press cake in a fixed-bed reactor: Part 2. Structural characterization of pyrolysis bio-oils. Bioresource Technology 99, 5498-5504.

SHAFIZADEH, F., (1982): Introduction to pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis 3, 283-305.

SHAFIZADEH, F., FU, Y.L., (1973): Pyrolysis of cellulose. Carbohydrate Research 29, 113-122.

SHAFIZADEH, F., FURNEAUX, R.H., COCHRAN, T.G., SCHOLL, J.P., SAKAI, Y., (1979): Production of levoglucosan and glucose from pyrolysis of cellulosic materials. Journal of Applied Polymer Science 23, 3525-3539.

SHAFIZADEH, F., MCGINNIS, G.D., PHILPOT, C.W., (1972): Thermal degradation of xylan and related model compounds. Carbohydrate Research 25, 23-33.

SHARMA, R.K., BAKHSHI, N.N., (1993): Catalytic upgrading of pyrolysis oil. Energy & Fuels 7, 306-314.

SHEN, D.K., GU, S., BRIDGWATER, A.V., (2010a): Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR. Journal of Analytical and Applied Pyrolysis 87, 199-206.

SHEN, D.K., GU, S., LUO, K.H., WANG, S.R., FANG, M.X., (2010b): The pyrolytic degradation of wood-derived lignin from pulping process. Bioresource Technology 101, 6136-6146.

SIPILA, K., KUOPPALA, E., FAGERNAS, L., OASMAA, A., (1998): Characterization of biomass-based flash pyrolysis oils. Biomass & Bioenergy 14, 103-113.

SJÖSTRÖM, E., (1993): Wood Chemistry: Fundamentals and Applications, 2nd Edition Edition. Academic Press Ltd, London.

SLUITER, J.B., RUIZ, R.O., SCARLATA, C.J., SLUITER, A.D., TEMPLETON, D.W., (2010): Compositional Analysis of Lignocellulosic Feedstocks. 1. Review and Description of Methods. Journal of Agricultural and Food Chemistry 58, 9043-9053.

SONOBE, T., WORASUWANNARAK, N., PIPATMANOMAI, S., (2008): Synergies in co-pyrolysis of Thai lignite and corncob. Fuel Processing Technology 89, 1371-1378.

STOCKER, M., (2008): Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials. Angew. Chem. Int. Ed. 47, 9200-9211.

STRADAL, J.A., UNDERWOOD, G.L., (1995): Process for producing hydroxyacetaldehyde PATENT, U.S.

TOFT, A.J., (1998): A comparison of integrated biomass to electricity systems. PhD Dissertation. Aston University, Birmingham.

TORIKAIU, K., UWANO, Y., NAKAMORI, T., TARORA, W., TAKAHASHI, H., (2004): Study on tobacco components involved in the pyrolytic generation of selected smoke constituents.

TORREGROSA-RODRÍGUEZ, P., MARTÍNEZ-ESCANDELL, M., RODRÍGUEZ-REINOSO, F., MARSH, H., DE SALAZAR, C.G., PALAZÓN, E.R., (2000): Pyrolysis of petroleum residues: II. Chemistry of pyrolysis. Carbon 38, 535-546.

TSAI, W.T., LEE, M.K., CHANG, Y.M., (2007): Fast pyrolysis of rice husk: Product yields and compositions. Bioresource Technology 98, 22-28.

TURLEY, D.B., (2008): The Chemical Value of Biomass. In: CLARK, J.H., DESWARTE, F.E.I. (Eds.) Introduction to Chemicals from Biomass. John Wiley & Sons, Ltd., York, pp. 21-46.

VAN DER HAGE, E.R.E., MULDER, M.M., BOON, J.J., (1993): Structural characterization of lignin polymers by temperature-resolved in-source pyrolysis--mass spectrometry and Curie-point pyrolysis--gas chromatography/mass spectrometry. Journal of Analytical and Applied Pyrolysis 25, 149-183.

VÁRHEGYI, G., ANTAL, M.J., JAKAB, E., SZABÓ, P., (1997): Kinetic modeling of biomass pyrolysis. Journal of Analytical and Applied Pyrolysis 42, 73-87.

VARHEGYI, G., GRONLI, M.G., DI BLASI, C., (2004): Effects of sample origin, extraction, and hot-water washing on the devolatilization kinetics of chestnut wood. Industrial & Engineering Chemistry Research 43, 2356-2367.

VENDERBOSCH, R.H., PRINS, W., (2010): Fast pyrolysis technology development. Biofuels Bioproducts & Biorefining-Biofpr 4, 178-208.

VORHER, W., (1976): Entwicklung eines kontinuierlichen Pyrolyseverfahrens zum Abbau von Phenollignin mit dem Ziel der Ligninverwertung unter besonderer Berücksichtigung der Rückgewinnung von Phenol aus Ablaugen eines Phenolzellstoffprozesses. PhD Dissertation. Universität Hamburg, Hamburg.

WALLIS, A.F.A., WEARNE, R.H., (1997): Characterization of resin in radiata pine woods, bisulfite pulps and mill pitch samples. Appita Journal 50, 409-414.

WANG, C., MACHIDA, H., NAKAGAWA, N., TAKARADA, T., KATO, K., (1995): Catalytic pyrolysis of plant-biomass in a powder-particle fluidized-bed. Kagaku Kogaku Ronbunshu 21, 531-539.

WANG, D., CZERNIK, S., MONTANE, D., MANN, M., CHORNET, E., (1997): Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. Industrial & Engineering Chemistry Research 36, 1507-1518.

WANG, J., ZHANG, M.Q., CHEN, M.Q., MIN, F.F., ZHANG, S.P., REN, Z.W., YAN, Y.J., (2006): Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass. Thermochimica Acta 444, 110-114.

WARD, J.W., (1970): The nature of active sites on zeolites : XI. The effects of the silica-to-alumina ratio on the acidity and catalytic activity of synthetic faujasite-type zeolites. Journal of Catalysis 17, 355-358.

WERPY, T., PETERSEN, G. (2004): Top Value Added Chemicals from Biomass. Volume I — Results of Screening for Potential Candidates from Sugars and Synthesis Gas. In: Biomass, WERPY, T., PETERSEN, G., eds. (Oak Ridge, TN, Pacific Northwest National Laboratory (PNNL); National Renewable Energy Laboratory (NREL), Office of Biomass Program (EERE)), pp. 1-66.

WESTERHOF, R.J.M., BRILMAN, D.W.F., VAN SWAAIJ, W.P.M., KERSTEN, S.R.A., (2009): Effect of Temperature in Fluidized Bed Fast Pyrolysis of Biomass: Oil Quality Assessment in Test Units. Industrial & Engineering Chemistry Research 49, 1160-1168.

WILLFÖR, S., PRANOVICH, A., TAMMINEN, T., PULS, J., LAINE, C., SUURNÄKKI, A., SAAKE, B., UOTILA, K., SIMOLIN, H., HEMMING, J., HOLMBOM, B., (2009): Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides-A comparison between different hydrolysis and subsequent chromatographic analytical techniques. Industrial Crops and Products 29, 571-580.

WILLFÖR, S., SUNDBERG, A., PRANOVICH, A., HOLMBOM, B., (2005): Polysaccharides in some industrially important hardwood species. Wood Sci Technol 39, 601-617.

WILLIAMS, P.T., BESLER, S., (1996): The influence of temperature and heating rate on the pyrolysis of biomass. Renewable Energy 7, 233-250.

WILLIAMS, P.T., HORNE, P.A., (1994a): Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading. Biomass and Bioenergy 7, 223-236.

WILLIAMS, P.T., HORNE, P.A., (1994b): The role of metal-salts in the pyrolysis of biomass. Renewable Energy 4, 1-13.

WOJTOWICZ, M.A., BASSILAKIS, R., SMITH, W.W., Y. CARANGELO, R.M.C., (2003): Modeling the evolution of volatile species during tobacco pyrolysis. Journal of Analytical and Applied Pyrolysis 66, 235-261.

WYMAN, C.E., (1994): Ethanol from lignocellulosic biomass: Technology, economics, and opportunities. Bioresource Technology 50, 3-15.

YANG, H., YAN, R., CHEN, H., LEE, D.H., ZHENG, C., (2007): Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86, 1781-1788.

YANG, H.P., YAN, R., CHEN, H.P., ZHENG, C.G., LEE, D.H., LIANG, D.T., (2006): In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. Energy & Fuels 20, 388-393.

YANIK, J., KOMMAYER, C., SAGLAM, M., YUKSEL, M., (2007): Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. Fuel Processing Technology 88, 942-947.

YE, T., YUAN, L., CHEN, Y., KAN, T., TU, J., ZHU, X., TORIMOTO, Y., YAMAMOTO, M., LI, Q., (2009): High Efficient Production of Hydrogen from Bio-oil Using Low-temperature Electrochemical Catalytic Reforming Approach Over NiCuZn–Al_2O_3 Catalyst. Catalysis Letters 127, 323-333.

ZHANG, S.P., YAN, Y.J., REN, J.W., LI, T.C., (2003): Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. Energy Sources 25, 57-65.

ZHENG, S., HEYDENRYCH, H.R., JENTYS, A., LERCHER, J.A., (2002): Influence of Surface Modification on the Acid Site Distribution of HZSM-5†. The Journal of Physical Chemistry B 106, 9552-9558.

ZHENG, S., JENTYS, A., LERCHER, J.A., (2006): Xylene isomerization with surface-modified HZSM-5 zeolite catalysts: An in situ IR study. Journal of Catalysis 241, 304-311.

5 Appendices

Appendix 1- GC- detectable components in BCO.

		weight percent (dry basis)				
	Components	Beech	Spruce	Iroko	Albizia	Corn cob
	Acids	**8.2**	**2.6**	**6.7**	**7.1**	**9.1**
1.	Acetic acid	8.0	2.5	6.1	6.8	8.5
2.	Propionic acid	0.2	0.1	0.6	0.3	0.6
	Nonaromatic Aldehydes	**10.3**	**11.3**	**9.1**	**9.1**	**7.3**
3.	Acetaldehyde, hydroxy-	7.9	9.8	7.0	6.7	5.1
4.	Propionaldehyde, 3-hydroxy	1.4	0.9	0.8	1.0	0.9
5.	Butandial or Propanal	1.0	0.6	1.3	1.4	1.4
	Nonaromatic Ketones	**5.1**	**4.2**	**8.1**	**5.8**	**10.2**
6.	Acetol (Hydroxypropanone)	2.7	2.4	4.3	3.1	4.7
7.	Butanone, 1-hydroxy-2-	0.3	0.2	0.6	0.4	1.3
8.	Acetoin; Hydroxy-2-butanone, 3-	0.1	0.1	0.1	-	-
9.	Propanone, acetyloxy-2-	0.1	0.1	0.1	0.1	0.3
10.	Cyclopentene-1-one, 2-	0.2	0.1	0.3	0.2	0.4
11.	Cyclopentene-1-one, 2,3-dimethyl-2-	-	-	<0.0	-	0.1
12.	Cyclopentene-1-one, 2-methyl-2-	<0.0	<0.0	0.1	0.1	0.2
13.	Cyclopentene-1-one, 3-methyl-2-	<0.0	<0.0	0.1	<0.0	0.1
14.	Cyclopentene-1-one, 2-hydroxy-2-	1.2	0.9	1.4	1.2	1.9
15.	Cyclopentene-3-one, 2-hydroxy-1-methyl-1-	0.5	0.3	1.1	0.6	1.3
	Furans	**2.4**	**2.5**	**2.8**	**2.7**	**3.3**
16.	Furanone, 2(5H)-	0.6	0.5	0.7	0.6	0.6
17.	Furaldehyde, 2-	0.6	0.4	0.5	0.6	1.0
18.	Furaldehyde, 3-	-	-	-	-	0.1
19.	Furaldehyde, 5-methyl-2-	-	0.1	0.1	0.1	0.1
20.	Furaldehyde, 5-(hydroxymethyl)-, 2-		0.3	-	-	-
21.	Furan-2-one, 5-methyl-, (5H)-	0.1	<0.0	0.1	0.1	0.1
22.	Furan-2-one, 3-methyl-, (5H)-	0.1	0.1	0.1	0.1	-
23.	Furan-x-on, x,x-dihydro-x-methyl-	0.3	0.2	0.2	0.2	0.2
24.	Butyrolactone, γ-	0.1	0.1	0.2	0.2	0.2
25.	Butyrolactone, 2-hydroxy-, γ-	0.3	0.4	0.5	0.4	0.5
26.	Furan-2-one, 4-methyl-(5H)- NIST MQ 88	0.1	0.1	0.1	0.1	0.1
27.	Lactone derivative	0.3	0.3	0.3	0.5	0.4
28.	Lactone derivative	-	0.1	-	-	0.1
	Pyrans	**1.9**	**1.8**	**0.7**	**1.2**	**1.3**
29.	Maltol (Pyran-4-on, 3-Hydroxy-2-methyl-4H-)	-	-	0.2	0.1	0.3
30.	Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	1.5	0.9	0.5	1.0	0.9
31.	Pyran-4-one, 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	0.3	0.9	0.1	0.1	0.1
	Sugars	**3.3**	**5.3**	**2.3**	**2.6**	**3.4**
32.	Anhydro-ß-D-arabinofuranose, 1,5-	-	-	-	-	0.4
33.	Anhydro-ß-D-xylofuranose, 1,5-	0.2	-	-	-	0.6

34.	Anhydro-ß-D-glucopyranose, 1,6- (Levoglucosan)	2.4	4.5	1.1	1.4	1.2
35.	Dianhydro-α-D-glucopyranose, 1,4:3,6-	0.2	0.1	0.3	0.2	0.4
36.	poss: Anhydrosugar unknown	0.5	0.8	1.0	0.5	0.9
	Benzenes	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
37.	Toluene	0.1	0.1	0.1	0.1	0.1
	Catechols	**<0.0**	**<0.0**	**0.4**	**0.1**	**0.3**
38.	Hydroquinone (Benzene, 1,4-dihydroxy-)	<0.0	-	0.3	0.1	0.2
39.	Benzenediol, methyl-	-	-	0.1	0.1	0.1
	Lignin derived Phenols	**0.2**	0.4	**0.9**	**0.4**	**3.6**
40.	Phenol	<0.0	0.1	0.2	0.1	0.3
41.	Cresol, o-	<0.0	0.1	0.1	<0.0	0.1
42.	Cresol, p-	<0.0	<0.0	0.1	<0.0	0.1
43.	Cresol, m-	<0.0	<0.0	0.1	<0.0	0.1
44.	Phenol, 2,4-dimethyl-	0.1	0.1	0.1	0.1	<0.0
45.	Phenol, 4-ethyl-	-	-	<0.0	<0.0	0.3
46.	Phenol, ethyl-methyl-	-	-	-	-	<0.0
47.	Phenol, 4-vinyl-	-	-	0.3	<0.0	2.5
48.	Benzaldehyde, 4-hydroxy-	-	-	-	-	0.1
49.	Benzaldehyde, hydroxy-	0.1	0.1	0.1	0.1	0.1
	Guaiacols (Methoxy phenols)	**1.4**	**4.0**	**4.0**	**2.7**	**3.5**
50.	Guaiacol	0.2	0.4	0.8	0.5	0.5
51.	Guaiacol, 4-methyl-	0.1	0.4	0.3	0.2	0.2
52.	Guaiacol, 4-ethyl-	<0.0	0.1	0.1	0.1	0.2
53.	Guaiacol, 4-vinyl-	0.1	0.4	0.7	0.4	1.7
54.	Guaiacol, 4-allyl- (Eugenol)	0.1	0.2	0.1	0.1	0.1
55.	Guaiacol, 4-propyl-	-	<0.0	<0.0	<0.0	<0.0
56.	Guaiacol, 4-propenyl- cis (Isoeugenol)	0.2	0.3	0.3	0.2	0.1
57.	Guaiacol, 4-propenyl-(trans) (Isoeugenol)	0.2	0.5	0.6	0.4	0.2
58.	Vanillin	0.2	0.5	0.3	0.2	0.3
59.	Phenylacetaldehyde, 4-hydroxy-3-methoxy- (Homovanillin)	0.1	0.3	0.2	0.1	-
60.	Dihydroconiferyl alcohol	-	0.1	-	-	-
61.	Coniferyl alcohol, Isomer of	-	0.2	0.1	0.1	-
62.	Phenylethanone, 4-hydroxy-3-methoxy- (Acetoguajacone)	0.1	0.3	0.3	0.2	0.1
63.	Propioguaiacon	-	0.1	-	-	-
64.	Guaiacyl acetone	<0.0	0.1	0.1	<0.0	0.1
65.	Coniferylaldehyde	0.1	0.2	0.2	0.2	<0.0
	Syringols (Dimethoxy phenols)	**3.0**	**<0.0**	**3.0**	**3.3**	**1.2**
66.	Syringol	0.5	-	0.7	0.6	0.3
67.	Syringol, 4-methyl-	0.2	-	0.2	0.2	0.1
68.	Syringol, 4-ethyl-	0.1	-	0.1	0.1	<0.0
69.	Syringol, 4-vinyl-	0.3	-	0.5	0.5	0.2
70.	Syringol, 4-allyl-	0.1	-	0.2	0.1	0.1
71.	Syringol, 4-propyl-	0.1	-	0.1	0.1	-
72.	Syringol, 4-(1-Propenyl)-, cis	0.1	-	0.1	0.1	0.1

73.	Syringol, 4-(1-Propenyl)-, trans	0.3	-	0.3	0.4	0.2
74.	Syringaldehyde	0.3	-	0.2	0.3	<0.0
75.	Homosyringaldehyde	0.1	-	0.1	0.1	-
76.	Sinapyl alcohol, Isomer of	0.1	-	-	0.1	-
77.	Acetosyringone	0.2	-	0.2	0.2	0.1
78.	Propiosyringone	0.1	-	-	0.1	<0.0
79.	Syringylacetone	0.1	-	0.1	0.1	<0.0
80.	Sinapaldehyde (trans)	0.5	-	0.3	0.5	-
	Total	**36.3**	**32.7**	**38.7**	**35.7**	**44.0**

- Not detected

Appendix 2A – Normalised area of pyrolysis products at different temperatures

Beech

	Temperature °C						
Chemical product	400	450	500	550	600	650	700
Acids							
Acetic acid	459	424	433	410	365	362	288
Nonaromatic Aldehydes							
Propenal, 2- (Acrolein)	-	-	116	193	255	325	317
Acetaldehyde, hydroxy-	422	480	397	374	139	256	136
Methylglyoxal (Propanal-2-on)	235	208	219	220	201	170	110
Propionaldehyde, 3-hydroxy-	105	112	116	115	96	84	53
Nonaromatic Ketones							
Acetol (Hydroxypropanone)	182	168	165	162	103	141	105
Butanone, 1-hydroxy-2-	-	-	-	11	7.7	9.6	6.6
Butandione, 2,3-; (Diacetyl)	64	70	77	90	59	58	45
Butenal-2-one, 3-	97	51	31	19	13	7.4	4.8
3-Pentanone	49	38	44	42	35	26	14
Cyclopenten-1-one, 2-	-	18	24	28	28	29	29
Cyclopenten-1-one, 2-hydroxy-2-	105	94	99	103	68	74	44
Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	19	21	27	29	22	22	15
Furans							
Furanone, 3(2H)-	-	14	15	15	12	12	7.6
Furanone, 2(5H)-	93	84	85	69	51	34	19
Furaldehyde, 2-	70	63	67	65	61	47	37
Furaldehyde, 5-(hydroxymethyl)-, 2-	27	25	25	22	12	14	9.5
2(3H)-Furanone, dihydro-4-hydroxy-	40	29	22	17	12	8.6	5.4
Furan-x-on, x,x-dihydro-x-methyl-	46	41	41	37	23	14	-
5-(Hydroxymethyl)dihydro-2(3H)-furanone	69	52	46	39	22	22	9.3
poss: 2-Hydroxy-gamma-butyrolactone	20	17	16	14	11	10	5.1
Lactone derivative	21	11	8.5	4.3	2.4	4.6	4.2
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	175	153	126	96	52	30	8.4
Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	46	48	32	22	10	6.3	-
Sugars							
Anhydro-ß-D-arabinofuranose, 1,5-	8.4	7.5	6.4	4.7	3.4	5.2	-
Anhydro-ß-D-xylofuranose, 1,5-	-	-	-	-	-	-	-
Anhydro-ß-D-glucopyranose, 1,6-; (Levoglucosan)	151	156	182	177	153	142	93
Dianhydro-α-D-glucopyranose, 1,4:3,6-	16	13	12	9.7	8	6.3	4
Anhydrosugar unknown (unspecific MS-spectrum)	107	65	49	36	25	6.3	-
Benzenes							
poss: 1H-Indenol	-	-	-	3.3	6.5	9.8	15
Indene, 6-hydroxy-7-methoxy-, 1H-	9	-	20	19	12	-	-
Indene, 6-hydroxy-7-methoxy-, 2H-	16	20	28	28	19	8.2	-
Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	20	22	25	17	7.4	-	-
Catechols							
Hydroquinone; (Benzene, 1,4-dihydroxy-)	4.3	4	4.2	4.7	4.3	5.2	5.3

Aromatic Aldehydes							
Benzaldehyde, 2-hydroxy-; (Salicylaldehyd)	-	-	-	-	4.4	6.3	7.3
Lignin derived Phenols							
Phenol	5.8	7.1	9.7	14	18	28	44
Cresol, o-	-	6	8.2	11	13	20	28
Cresol, m-	-	-	-	6.3	8.5	7.9	22
Phenol, 4-ethyl-	-	-	-	-	2.3	3.7	6.2
Phenol, 4-vinyl-	-	-	-	-	4.4	6.9	12
Guaiacols (Methoxy phenols)							
Guaiacol	43	37	35	29	16	9.2	6.3
Guaiacol, 4-methyl-	19	16	19	14	6.9	4.4	-
Guaiacol, 4-vinyl-	49	46	50	44	26	12	-
Guaiacol, 4-allyl-; (Eugenol)	11	12	14	13	7.7	4.1	-
Guaiacol, 4-propenyl- (trans); (Isoeugenol)	49	33	40	33	21	11	-
Vanillin	18	20	24	25	21	13	5.5
Phenylacetaldehyde, 4-hydroxy-3-methoxy;- (Homovanillin)	17	19	23	14	12	5.6	-
Coniferyl alcohol (trans)	46	63	69	53	19	0	-
Phenylethanone, 4-hydroxy-3-methoxy-; (Acetoguajacone)	10	12	15	14	11	6	-
Coniferylaldehyde	15	15	19	16	9.6	2.7	-
Syringols (Dimethoxy phenols)							
Syringol	71	67	68	50	22	7.9	-
Syringol, 4-methyl-	42	39	41	28	12	6	-
Syringol, 4-vinyl-	124	111	105	78	37	14	-
Syringol, 4-allyl-	17	18	23	16	8	3.9	-
Syringol, 4-(1-propenyl)-, trans	82	78	81	53	21	6.4	-
Syringaldehyde	41	50	58	55	37	17	3.7
Sinapyl alcohol (trans)	46	61	47	25	3.9	-	-
Acetosyringone	24	28	32	26	21	12	-
Syringylacetone	29	23	19	16	8.4	4.1	-
Sinapaldehyde (trans)	80	74	71	55	27	7.1	-

Appendix 2B - Normalised area of pyrolysis products at different temperatures

Spruce

	Temperature °C						
Chemical product	400	450	500	550	600	650	700
Acids							
Acetic acid	160	144	139	134	133	119	114
Alkene	**-**	**-**	**-**	**-**	**-**	**-**	**-**
poss: 1,5-Heptadiene, 2,6-dimethyl-	-	-	-	-	-	-	-
poss: 1,6-Dimethylhepta-1,3,5-triene	-	-	-	-	-	-	-
Cyclohexene,3-(2-propenyl)-	-	-	-	-	-	-	-
Nonaromatic Aldehydes							
Propenal, 2- (Acrolein)	-	-	127	205	284	305	340
Acetaldehyde, hydroxy-	486	518	470	426	295	176	186
Methylglyoxal (Propanal-2-on)	222	235	223	225	213	175	116
Propionaldehyde, 3-hydroxy-	65	72	72	71	63	50	37
Nonaromatic Ketones							
Acetol (Hydroxypropanone)	150	148	134	130	123	106	113
Butanone, 1-hydroxy-2-	-	-	-	0	7.4	6.8	6.8
Butandione, 2,3-; (Diacetyl)	-	73	73	84	60	53	48
Butenal-2-one, 3-	-	25	29	21	11	5.2	4.2
3-Pentanone	-	-	-	-	-	-	-
Cyclopenten-1-one, 2-	-	16	20	24	27	28	8.8
Cyclopenten-1-one, 2-hydroxy-2-	80	82	85	86	81	63	49
Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	-	16	19	20	22	18	13
Furans							
Furanone, 3(2H)-	-	15	15	14	15	12	8.4
Furanone, 2(5H)-	72	68	69	57	43	29	19
Furaldehyde, 2-	46	47	50	52	48	41	34
Furaldehyde, 5-(hydroxymethyl)-, 2-	65	66	60	58	43	30	22
2(3H)-Furanone, dihydro-4-hydroxy-	62	46	28	18	3.8	12	7.9
Furan-x-on, x,x-dihydro-x-methyl-	36	33	35	30	21	9.6	-
5-(Hydroxymethyl)dihydro-2(3H)-furanone	59	46	36	31	22	13	7.8
poss: 2-Hydroxy-gamma-butyrolactone	19	16	14	12	12	9.5	-
Lactone derivative	22	12	12	12	2	8.6	8.5
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	91	84	70	54	35	12	5.1
Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	138	121	74	60	24	-	-
Sugars							
Anhydro-ß-D-arabinofuranose, 1,5-	20	18	15	13	9.1	8	-
Anhydro-ß-D-xylofuranose, 1,5-	-	-	-	-	-	-	-
Anhydro-ß-D-glucopyranose, 1,6-; (Levoglucosan)	260	298	298	291	281	234	165
Dianhydro-α-D-glucopyranose, 1,4:3,6-	9.6	8.5	8.2	7.6	6.2	4.6	3.4
Anhydrosugar unknown (unspecific MS-spectrum)	79	53	33	25	22	9.3	6.6
Benzenes							
poss: 1H-Indenol	-	-	-	5.8	12	18	-
Indene, 6-hydroxy-7-methoxy-, 1H-	23	25	32	28	15	4.9	-
Indene, 6-hydroxy-7-methoxy-, 2H-	30	32	38	34	19	-	-

Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	-	-	-	-	-	-	-
Catechols							
Hydroquinone; (Benzene, 1,4-dihydroxy-)	-	-	-	3.1	3.6	4.5	4.9
Aromatic Aldehydes							
Benzaldehyde, 2-hydroxy-; (Salicylaldehyd)	-	-	-	3.5	6.8	7.7	9.9
Lignin derived Phenols							
Phenol	-	9.7	12	17	25	38	68
Cresol, o-	-	9.4	11	14	19	25	36
Cresol, m-	-	4.9	6	7.6	11	17	26
Phenol, 4-ethyl-	-	-	3.8	3.9	5.3	7.2	13
Phenol, 4-vinyl-	-	-	5.1	6.9	9.5	16	28
Guaiacols (Methoxy phenols)							
Guaiacol	86	88	81	60	32	12	3.2
Guaiacol, 4-methyl-	91	98	88	59	26	6.6	-
Guaiacol, 4-vinyl-	107	116	116	102	57	21	-
Guaiacol, 4-allyl-; (Eugenol)	22	30	33	30	17	6.8	-
Guaiacol, 4-propenyl- (trans); (Isoeugenol)	95	103	104	83	52	18	-
Vanillin	54	60	64	69	45	22	7.8
Phenylacetaldehyde, 4-hydroxy-3-methoxy;- (Homovanillin)	25	28	30	29	15	5.1	-
Coniferyl alcohol (trans)	121	115	164	120	51	-	-
Phenylethanone, 4-hydroxy-3-methoxy-; (Acetoguajacone)	27	32	35	34	22	9	2.7
Coniferylaldehyde	92	90	87	76	48	16	3.2

Appendix 2C - Normalised area of pyrolysis products at different temperatures

Iroko

Chemical product	Temperature °C 400	450	500	550	600	650	700
Acids							
Acetic acid	214	205	200	193	198	161	149
Alkene	-	-	-	-	-	-	-
poss: 1,5-Heptadiene, 2,6-dimethyl-	52	52	51	34	21	-	-
poss: 1,6-Dimethylhepta-1,3,5-triene	32	14	22	17	12	4.4	-
Cyclohexene,3-(2-propenyl)-	-	-	13	10	12	8.1	4.4
Nonaromatic Aldehydes							
Propenal, 2- (Acrolein)	-	-	-	84	136	151	185
Acetaldehyde, hydroxy-	320	293	246	191	148	93	95
Methylglyoxal (Propanal-2-on)	153	131	134	133	136	99	60
Propionaldehyde, 3-hydroxy-	47	49	49	47	46	32	25
Nonaromatic Ketones							
Acetol (Hydroxypropanone)	199	193	173	153	142	106	100
Butanone, 1-hydroxy-2-	18	19	20	19	18	12	11
Butandione, 2,3-; (Diacetyl)	45	47	56	49	52	43	33
Butenal-2-one, 3-	18	20	17	14	7.8	3.3	0
3-Pentanone	69	61	57	49	44	27	15
Cyclopenten-1-one, 2-	12	17	22	26	29	26	26
Cyclopenten-1-one, 2-hydroxy-2-	132	116	98	83	75	51	39
Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	29	34	39	41	39	28	22
Furans							
Furanone, 3(2H)-	38	26	18	12	8.7	5.2	4.4
Furanone, 2(5H)-	75	67	56	46	37	22	13
Furaldehyde, 2-	36	39	40	41	41	31	24
Furaldehyde, 5-(hydroxymethyl)-, 2-	8.1	8.2	7.8	6.2	5.4	4.6	5.1
2(3H)-Furanone, dihydro-4-hydroxy-	19	17	18	16	12	-	-
Furan-x-on, x,x-dihydro-x-methyl-	27	23	19	16	12	4.9	-
5-(Hydroxymethyl)dihydro-2(3H)-furanone	40	29	20	14	12	6.2	-
poss: 2-Hydroxy-gamma-butyrolactone	16	14	13	12	12	8.3	-
Lactone derivative	16	14	13	9.2	9.7	2.2	6.5
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	43	37	27	20	14	6.3	1.9
Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	7.1	6.6	4.9	3.5	-	-	-
Sugars							
Anhydro-ß-D-arabinofuranose, 1,5-	5.1	4.1	3.6	3.4	3.7	-	-
Anhydro-ß-D-xylofuranose, 1,5-	-	-	-	-	-	-	-
Anhydro-ß-D-glucopyranose, 1,6-; (Levoglucosan)	32	37	42	43	35	40	29
Dianhydro-α-D-glucopyranose, 1,4:3,6-	8.6	8.2	7.8	7	6.9	5.5	3.9
Anhydrosugar unknown (unspecific MS-spectrum)	147	97	66	43	34	9.8	8.9
Benzenes							
poss: 1H-Indenol	-	-	-	-	9.2	11	6.1
Indene, 6-hydroxy-7-methoxy-, 1H-	7.7	12	23	22	15	-	-
Indene, 6-hydroxy-7-methoxy-, 2H-	10	15	26	27	21	-	-

Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	7.4	11	14	10	5.5	-	-
Catechols							
Hydroquinone; (Benzene, 1,4-dihydroxy-)	6.1	5.5	5.7	6	6.3	6.1	7.3
Aromatic Aldehydes							
Benzaldehyde, 2-hydroxy-; (Salicylaldehyd)	-	-	-	-	-	8.4	7.9
Lignin derived Phenols							
Phenol	19	24	24	28	37	41	62
Cresol, o-	9.3	12	14	17	23	25	33
Cresol, m-	6.2	7.4	8	9.3	15	18	26
Phenol, 4-ethyl-	-	-	-	4.6	8.2	10	14
Phenol, 4-vinyl-	67	72	70	66	75	65	66
Guaiacols (Methoxy phenols)							
Guaiacol	89	94	88	70	40	14	-
Guaiacol, 4-methyl-	37	40	41	30	17	3.7	-
Guaiacol, 4-vinyl-	150	155	146	114	67	21	4
Guaiacol, 4-allyl-; (Eugenol)	15	18	21	17	11	3.5	-
Guaiacol, 4-propenyl- (trans); (Isoeugenol)	66	77	77	62	41	-	-
Vanillin	18	21	23	23	19	9	4
Phenylacetaldehyde, 4-hydroxy-3-methoxy;- (Homovanillin)	9.8	9.9	11	9	4.6	-	-
Coniferyl alcohol (trans)	123	136	108	80	31	-	-
Phenylethanone, 4-hydroxy-3-methoxy-; (Acetoguajacone)	15	17	18	17	14	6.6	-
Coniferylaldehyde	22	22	-	18	9.3	6.4	-
Syringols (Dimethoxy phenols)							
Syringol	66	67	62	43	21	4.7	-
Syringol, 4-methyl-	27	30	27	18	8.8	-	-
Syringol, 4-vinyl-	138	134	118	82	39	9.2	-
Syringol, 4-allyl-	15	17	18	13	6.7	-	-
Syringol, 4-(1-propenyl)-, trans	59	62	56	38	17	4.1	-
Syringaldehyde	14	15	16	15	11	4.4	-
Sinapyl alcohol (trans)	27	28	20	11	-	-	-
Acetosyringone	14	14	15	14	11	6.2	-
Syringylacetone	16	20	40	14	11	-	-
Sinapaldehyde (trans)	25	24	27	20	7.9	-	-

Appendix 2D - Normalised area of pyrolysis products at different temperatures

Albizia

	Temperature °C						
Chemical product	400	450	500	550	600	650	700
Acids							
Acetic acid	274	272	272	269	254	217	206
Nonaromatic Aldehydes							
Propenal, 2- (Acrolein)	-	53	94	140	187	217	240
Acetaldehyde, hydroxy-	223	255	188	170	145	91	83
Methylglyoxal (Propanal-2-on)	152	132	156	161	159	143	105
Propionaldehyde, 3-hydroxy-	47	52	58	57	50	42	34
Nonaromatic Ketones							
Acetol (Hydroxypropanone)	128	134	134	125	117	88	93
Butanone, 1-hydroxy-2-	12	15	16	16	15	9.3	10
Butandione, 2,3-; (Diacetyl)	47	49	66	54	52	46	41
Butenal-2-one, 3-	17	23	28	21	10	5.6	4.2
3-Pentanone	80	75	67	61	49	32	20
Cyclopenten-1-one, 2-	12	16	22	24	25	24	25
Cyclopenten-1-one, 2-hydroxy-2-	109	103	93	83	71	49	40
Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	18	23	30	28	26	18	16
Furans							
Furanone, 3(2H)-	11	13	13	13	12	9.1	6.4
Furanone, 2(5H)-	73	65	70	58	44	31	17
Furaldehyde, 2-	47	43	48	47	41	34	26
Furaldehyde, 5-(hydroxymethyl)-, 2-	11	12	9.6	8.3	6.1	4.4	5
2(3H)-Furanone, dihydro-4-hydroxy-	25	22	-	-	-	8.8	5.7
Furan-x-on, x,x-dihydro-x-methyl-	28	24	24	20	16	9.1	-
poss: 2-Hydroxy-gamma-butyrolactone	16	14	15	13	11	8	-
Lactone derivative	67	60	41	33	25	12	7
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	95	84	72	56	37	18	5.8
Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	12	12	8	6.8	4.4	-	-
Sugars							
Anhydro-ß-D-arabinofuranose, 1,5-	6.9	7	6.6	6.9	6.5	-	-
Anhydro-ß-D-glucopyranose, 1,6-; (Levoglucosan)	70	80	94	93	86	63	58
Dianhydro-α-D-glucopyranose, 1,4:3,6-	8.2	7.7	8	7	6.7	4.9	3.8
Benzenes							
poss: 1H-Indenol	-	-	-	4	6.9	11	13
Indene, 6-hydroxy-7-methoxy-, 1H-	7.8	9.4	23	27	15	4.5	-
Indene, 6-hydroxy-7-methoxy-, 2H-	9.1	12	26	34	22	11	7.8
Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	13	15	24	18	6.7	-	-
Catechols							
Hydroquinone; (Benzene, 1,4-dihydroxy-)	4.2	4.1	4.4	4.6	5	4.7	5.7
Aromatic Aldehydes							
Benzaldehyde, 2-hydroxy-; (Salicylaldehyd)	-	-	-	-	7	6.9	7.1

Lignin derived Phenols							
Phenol	8.4	11	15	17	23	31	45
Cresol, o-	5.4	7.1	9.7	11	16	19	29
Cresol, m-	-	4.7	5.6	7	12	17	25
Phenol, 4-ethyl-	-	-	-	-	3.9	5.1	7.4
Phenol, 4-vinyl-	3.2	4.6	4.4	5.8	7	9.2	15
Guaiacols (Methoxy phenols)							
Guaiacol	69	74	75	54	30	14	-
Guaiacol, 4-methyl-	25	29	29	22	12	5.7	-
Guaiacol, 4-vinyl-	83	88	86	72	42	19	5.2
Guaiacol, 4-allyl-; (Eugenol)	12	15	18	16	8.9	3.8	-
Guaiacol, 4-propenyl- (trans); (Isoeugenol)	68	75	81	66	41	25	-
Vanillin	12	14	18	19	16	12	5
Phenylacetaldehyde, 4-hydroxy-3-methoxy;- (Homovanillin)	5.5	7.4	-	7	3.5	-	-
Coniferyl alcohol (trans)	116	114	113	71	31	-	-
Phenylethanone, 4-hydroxy-3-methoxy-; (Acetoguajacone)	9.1	11	14	14	9.9	5.8	-
Coniferylaldehyde	19	20	21	19	-	2.9	-
Syringols (Dimethoxy phenols)							
Syringol	96	105	98	71	31	9.6	-
Syringol, 4-methyl-	38	44	43	29	13	5.3	-
Syringol, 4-vinyl-	153	151	134	94	44	16	-
Syringol, 4-allyl-	16	18	21	18	7.7	5.1	-
Syringol, 4-(1-propenyl)-, trans	102	108	98	61	26	6.9	-
Syringaldehyde	21	26	31	31	21	13	-
Sinapyl alcohol (trans)	50	53	40	16	3.3	-	-
Acetosyringone	17	20	22	19	13	8.1	-
Syringylacetone	25	23	20	15	19	4.9	-
Sinapaldehyde (trans)	47	46	47	33	16	-	-

Appendix 2E - Normalised area of pyrolysis products at different temperatures
Corncob

	Temperature °C						
Chemical product	400	450	500	550	600	650	700
Acids							
Acetic acid	268	255	256	261	242	232	194
Nonaromatic Aldehydes							
Propenal, 2- (Acrolein)	-	-	-	130	193	260	263
Acetaldehyde, hydroxy-	318	324	281	252	198	208	99
Methylglyoxal (Propanal-2-on)	208	237	244	263	244	208	131
Propionaldehyde, 3-hydroxy-	49	55	58	59	54	49	32
Nonaromatic Ketones							
Acetol (Hydroxypropanone)	217	223	213	203	183	186	130
Butanone, 1-hydroxy-2-	21	23	25	24	21	20	13
Butandione, 2,3-; (Diacetyl)	49	64	82	76	80	76	58
Butenal-2-one, 3-	19	25	26	24	12	4.5	3.1
3-Pentanone	92	88	81	72	60	41	23
Cyclopenten-1-one, 2-	15	22	27	32	34	34	32
Cyclopenten-1-one, 2-hydroxy-2-	139	129	121	117	102	89	52
Cyclopenten-3-one, 2-hydroxy-1-methyl-1-	29	36	42	44	40	33	23
Furans							
Furanone, 3(2H)-	13	16	17	17	17	15	9.3
Furanone, 2(5H)-	73	71	69	65	45	30	17
Furaldehyde, 2-	61	60	63	66	59	50	37
Furaldehyde, 5-(hydroxymethyl)-, 2-	11	12	10	9.4	7.2	7.2	5
2(3H)-Furanone, dihydro-4-hydroxy-	14	12	9.4	8.7	6.5	5.1	-
Furan-x-on, x,x-dihydro-x-methyl-	37	35	30	26	18	10	2.1
poss: 2-Hydroxy-gamma-butyrolactone	15	15	16	20	24	26	24
Lactone derivative	65	55	42	34	21	16	5
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	80	74	57	47	29	16	2.1
Pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	7.2	7.3	5.3	4.5	-	-	-
Sugars							
Anhydro-ß-D-arabinofuranose, 1,5-	36	33	32	26	17	12	7.6
Anhydro-ß-D-xylofuranose, 1,5-	39	44	43	41	33	25	10
Anhydro-ß-D-glucopyranose, 1,6-; (Levoglucosan)	44	61	59	59	55	47	26
Dianhydro-α-D-glucopyranose, 1,4:3,6-	13	12	13	12	9.7	8.3	5.6
Benzenes							
poss: 1H-Indenol	-	-	-	-	4.1	6.3	7.5
Indene, 6-hydroxy-7-methoxy-, 1H-	2.8	5	7.1	10	5.5	-	-
Indene, 6-hydroxy-7-methoxy-, 2H-	3	5.5	8	-	7.3	-	-
Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	-	5.3	5.8	5.3	2	-	-
Catechols							
Hydroquinone; (Benzene, 1,4-dihydroxy-)	9.1	9.1	8.8	9.7	9.3	13	10
Aromatic Aldehydes							
Benzaldehyde, 2-hydroxy-; (Salicylaldehyd)	3.9	4.5	4.5	4.7	4.8	6.5	5.1

Lignin derived Phenols							
Phenol	26	32	34	35	43	53	71
Cresol, o-	5	12	8.4	10	18	22	24
Cresol, m-	5.5	6.6	7.5	9.4	10	15	16
Phenol, 4-ethyl-	4.7	6.2	7.7	11	15	21	25
Phenol, 4-vinyl-	283	305	298	306	282	290	235
Guaiacols (Methoxy phenols)							
Guaiacol	51	56	56	45	25	11	5.9
Guaiacol, 4-methyl-	12	14	15	13	7.5	-	-
Guaiacol, 4-vinyl-	178	193	194	161	89	35	-
Guaiacol, 4-allyl-; (Eugenol)	-	5.9	5.8	5.5	3.9	-	-
Vanillin	23	26	27	27	19	12	3.4
Coniferyl alcohol (trans)	15	16	18	-	-	-	-
Phenylethanone, 4-hydroxy-3-methoxy-; (Acetoguajacone)	2.7	4	4.2	3.8	3	1.7	-
Coniferylaldehyde	5.8	5.1	4.7	4.1	2.9	-	-
Syringols (Dimethoxy phenols)							
Syringol	34	37	35	25	11	3.7	7.5
Syringol, 4-methyl-	7.5	10	9.6	8.3	5.6	5.1	-
Syringol, 4-vinyl-	29	31	29	22	10	3.1	-
Syringol, 4-allyl-	-	4.9	5.1	3.9	2.3	-	-
Syringol, 4-(1-propenyl)-, trans	22	24	22	15	6.6	1.9	-
Syringaldehyde	4.6	5.5	-	5.5	3.6	2	-
Acetosyringone	4.3	5.1	5.7	4.8	3.8	2.7	-
Syringylacetone	4.7	5.1	4.6	3.8	1.8	-	-
Sinapaldehyde (trans)	5.6	5.1	3.9	-	-	-	-

Eidesstattliche Versicherung

I hereby declare that I have independently carried out this present work without any external assistance other than the acknowledged and specified sources and equipment and that the work has not been verbatim or in substance plagiarised from acknowledged or otherwise published works.

I certify that I am neither registered for PhD programme at another university nor have I submitted this dissertation at another university.

Hamburg, June 2011

Mayowa Akeem Azeez

Appendix 3A - Normalised area of pyrolysis products of treated and untreated samples.

			Treated beech with			
R.T.	Chemical product	Beech	H_2O	HCl	$CaCl_2$	NaCl
4.51	Acrolein (2-Propenal)	170	191	135	148	133
4.71	Propanal-2-one; Methylglyoxal	276	307	187	300	248
5.96	Butandione, 2,3- (Diacetyl)	94	97	69	87	88
6.40	3-Pentanone	48	24	10	21	60
7.12	Acetaldehyde, hydroxy-	548	595	263	561	742
7.91	Butenal-2; Crotonaldehyde trans	56	51	23	48	48
8.17	Acetic acid	562	541	448	546	591
9.66	Acetol (Hydroxypropanone)	198	124	48	107	287
13.71	Ethyleneglycol	26	44	5	55	33
14.39	Propionaldehyde, 3-hydroxy	147	151	125	155	154
14.93	Furanone, 2(3H)-	45	37	21	29	39
16.60	Oxopropanoic acid methylester, 2-	134	90	9	73	116
16.65	Propanal	96	51	32	35	125
17.36	Furaldehyde, 2-	91	98	120	98	72
22.99	Cyclopentene-1-one, 2-hydroxy-2-	123	83	42	79	130
24.02	Furan-x-one, x,x-Dihydro-x-methyl-	49	51	45	49	44
25.94	Furanone, 2(5H)-	122	77	34	62	114
27.02	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	164	243	151	268	146
27.88	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	31	16	8	20	41
30.41	Guaiacol	37	29	29	32	46
34.26	5-(Hydroxymethyl)dihydro-2(3H)-furanone	52	40	17	23	54
41.10	Anhydro-ß-D-arabinofuranose, 1,5-	3	9	20	10	3
41.65	Guaiacol, 4-vinyl-	61	52	47	52	69
43.40	Furaldehyde, 5-(hydroxymethyl)-2-	36	76	85	79	27
43.91	Syringol	78	43	52	52	106
44.99	Furanone, dihydro-4-hydroxy-2(3H)-	34	27	13	22	29
46.27	Pyran-4-one, 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	46	138	202	132	31
47.63	Syringol, 4-methyl	43	55	76	52	39
48.68	Indene, 6-Hydroxy-7-methoxy-1H-	54	36	33	31	28
49.09	Indene, 6-Hydroxy-7-methoxy-, 2H-	60	31	27	38	39
50.44	Phenylacetaldehyde, 4-hydroxy-3-methoxy- (Homovanillin)	28	31	41	29	23
52.84	Syringol, 4-vinyl	133	99	86	106	171
56.81	Indene, 6-hydroxy-5,7-dimethoxy-1H-	59	33	33	36	29
57.12	Anhydro-ß-D-glucopyranose (Levoglucosan)	228	633	2040	730	130
57.73	Syringol, 4-(1-Propenyl)- trans	88	88	83	92	17
58.71	Syringaldehyde	76	81	71	67	65
60.25	Homosyringaldehyde	23	32	43	28	23
61.89	Coniferyl alcohol trans	34	16	18	15	
62.56	Coniferyl aldehyde	25	22	78	21	23
70.92	Sinapaldehyde	63	71	64	68	69

Appendix 3B - Normalised area of pyrolysis products of treated and untreated samples.

			Treated spruce with			
R.T.	Chemical product	Spruce	H_2O	HCl	$CaCl_2$	NaCl
4.48	Acrolein (2-Propenal)	124	117	121	91	65
4.66	Methylglyoxal (Propanal-2-one)	179	199	175	224	149
5.91	Butandione, 2,3- (Diacetyl)	83	79	88	79	77
6.36	3-Pentanone	25	13	11	14	33
7.08	Acetaldehyde, hydroxy-	636	602	282	474	730
8.11	Acetic acid	164	139	135	159	194
9.61	Acetol (Hydroxypropanone)	157	98	48	92	293
10.84	Ethene, 1,2-dihydroxy-	19	21	13	16	10
13.13	2-Propenoic acid, 2-hydroxyethyl ester	26	25	15	22	23
14.34	Propionaldehyde, 3-hydroxy	88	78	43	72	85
14.89	Butenal-2-one, 3-	32	24	24	20	38
14.99	Furanone, 2(3H)-	56	25	12	13	64
15.65	Furanone, 3(2H)	17	15	33	20	18
16.56	Prob. Oxopropanoic acid methylester, 2-	128	71	15	69	115
16.60	Propanal	70	44	34	33	136
17.32	Furaldehyde, 2-	61	64	92	68	50
22.95	Cyclopentene-1-one, 2-hydroxy-2-	99	70	50	74	147
23.98	Furan-x-one, x,x-dihydro-x-methyl-	38	29	25	34	39
25.90	Furanone, 2(5H)-	91	53	47	50	120
26.96	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	88	110	97	116	47
27.84	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	18	14	12	24	40
29.77	Phenol	16	14	19	18	20
30.39	Guaiacol	86	65	67	79	145
35.28	Guaiacol, 4-methyl	97	107	139	122	80
41.10	Anhydro-ß-D-arabinofuranose, 1,5-	15	19	25	20	10
41.65	Guaiacol, 4-vinyl-	135	113	110	125	182
43.41	Furaldehyde, 5-(hydroxymethyl)-2-	89	117	101	104	43
46.30	Pyran-4-one, 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	118	197	152	101	33
47.26	Guaiacol, 4-propenyl- ; (Isoeugenol) trans	112	107	104	136	123
48.09	Vanillin	77	74	59	51	53
48.68	Indene, 6-Hydroxy-7-methoxy-1H-	46	38	47	44	32
49.09	Indene, 6-Hydroxy-7-methoxy-, 2H-	45	35	47	40	38
50.45	Phenylacetaldehyde, 4-hydroxy-3-methoxy- (Homovanillin)	37	42	39	29	29
57.24	Anhydro-ß-D-glucopyranose (Levoglucosan)	331	602	1267	743	118
58.95	Coniferyl alcohol (cis)	23	9	10	8	35
61.93	Coniferyl alcohol trans	145	73	39	43	210
62.60	Coniferyl aldehyde	104	89	102	77	100

Appendix 3C - Normalised area of pyrolysis products of treated and untreated samples.

			Treated iroko with			
R.T.	Chemical product	iroko	H_2O	HCl	$CaCl_2$	NaCl
4.46	Acrolein (2-Propenal)	41	90	80	64	44
4.66	Propanal-2-one; Methylglyoxal	101	143	135	145	116
5.92	Butandione, 2,3- (Diacetyl)	60	66	66	40	65
6.33	3-Pentanone	40	28	15	16	36
7.06	Acetaldehyde, hydroxy-	357	435	358	417	398
7.85	Butenal-2; Crotonaldehyde trans	18	31	23	0	21
8.10	Acetic acid	247	224	206	223	249
9.61	Acetol (Hydroxypropanone)	209	137	76	107	209
13.48	1,5-Heptadiene, 2,6-dimethyl-	51	56	61	63	54
13.65	Ethyleneglycol	24	44	24	46	30
14.09	Butanone, 1-hydroxy-2-	20	12	6	9	17
14.33	Propionaldehyde, 3-hydroxy	53	75	59	70	64
14.89	Furanone, 2(3H)-	21	21	21	16	0
14.99	Butenal-2-one, 3-	26	21	14	13	28
16.54	Oxopropanoic acid methylester, 2-	62	90	60	66	66
16.60	Butandial or Propanal	119	55	46	36	99
17.32	Furaldehyde, 2-	42	54	73	51	43
21.80	Cyclopentene-1,4-dione, 2-	17	16	15	14	17
22.96	Cyclopentene-1-one, 2-hydroxy-2-	107	85	55	73	95
23.98	Furan-x-one, x,x-Dihydro-x-methyl-	21	31	31	28	23
25.89	Furanone, 2(5H)-	76	62	49	42	77
26.95	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	29	119	191	171	47
27.84	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	44	28	14	28	43
29.77	Phenol	27	19	19	20	26
30.39	Guaiacol	99	60	58	55	99
34.24	(S)-(+)-2',3'-Dideoxyribonolactone	21	20	21	13	17
35.27	Guaiacol, 4-methyl	39	62	87	64	45
41.65	Guaiacol, 4-vinyl-	162	133	119	127	169
41.78	Phenol, 4-vinyl	0	80	61	74	79
43.90	Syringol	62	35	32	28	65
44.99	Guaiacol, 4-propenyl-; (Isoeugenol) cis	22	29	26	23	25
47.26	Guaiacol, 4-propenyl- ; (Isoeugenol) trans	83	95	77	97	91
47.62	Syringol, 4-methyl	30	44	57	42	33
49.73	Resorcinol	55	56	54	50	49
52.84	Syringol, 4-vinyl	133	102	80	97	145
53.46	Syringol, 4-allyl-	21	22	21	20	22
57.07	Anhydro-ß-D-glucopyranose (Levoglucosan)	51	247	451	311	60
57.73	Syringol, 4-(1-Propenyl)- trans	62	65	58	60	66
58.70	Syringaldehyde	19	27	24	20	21
61.92	Coniferyl alcohol trans	111	82	40	34	120
62.58	Coniferyl aldehyde	28	35	48	32	31
70.93	Sinapaldehyde	25	29	31	28	29

Appendix 3D - Normalised area of pyrolysis products of treated and untreated samples.

			Treated albizia with			
R.T.	Chemical product	Albizia	H_2O	HCl	$CaCl_2$	NaCl
4.52	Acrolein (2-Propenal)	102	126	115	121	115
4.72	Methylglyoxal (Propanal-2-one)	184	214	172	228	182
5.97	Butandione, 2,3- (Diacetyl)	76	79	66	78	78
6.40	3-Pentanone	80	36	14	28	67
7.12	Acetaldehyde, hydroxy-	377	446	259	343	333
8.17	Acetic acid	407	372	326	374	384
9.67	Acetol (Hydroxypropanone)	194	132	53	98	191
13.70	Ethyleneglycol	8	16	3	24	11
14.14	Butanone, 1-hydroxy-2-	19	7	4	6	16
14.38	Propionaldehyde, 3-hydroxy	71	89	75	95	80
14.93	Furanone, 2(3H)-	32	32	20	28	29
15.04	Butenal-2-one, 3-	21	23	6	7	19
16.59	Oxopropanoic acid methylester, 2-	89	89	14	68	73
16.66	Butandial or Propanal	150	78	34	39	120
17.36	Furaldehyde, 2-	64	69	91	84	66
23.00	Cyclopentene-1-one, 2-hydroxy-2-	132	91	47	86	113
24.02	Furan-x-one, x,x-Dihydro-x-methyl-	29	38	36	38	24
25.94	Furanone, 2(5H)-	108	87	39	66	93
27.01	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	103	193	195	209	85
27.88	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	36	18	8	24	39
29.79	Phenol	18	14	12	15	22
30.41	Guaiacol	90	53	54	56	94
34.28	(S)-(+)-2',3'-Dideoxyribonolactone	56	47	28	20	25
35.29	Guaiacol, 4-methyl	38	45	70	53	36
41.12	Anhydro-ß-D-arabinofuranose, 1,5-	6	12	24	13	5
41.66	Guaiacol, 4-vinyl-	114	93	96	97	119
43.41	Furaldehyde, 5-(hydroxymethyl)-2-	17	38	65	45	13
43.91	Syringol	126	65	68	56	128
45.00	Furanone, dihydro-4-hydroxy-2(3H)-	32	35	17	26	27
46.26	Pyran-4-one, 2-Hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-	14	63	146	38	10
47.27	Guaiacol, 4-propenyl-; (Isoeugenol) cis	101	100	78	92	97
47.63	Syringol, 4-methyl	53	60	92	68	49
49.09	Indene, 6-Hydroxy-7-methoxy-, 2H-	40	29	25	37	47
52.85	Syringol, 4-vinyl	177	128	118	135	188
55.40	Syringol, 4-(1-Propenyl)- cis	26	22	23	26	25
57.13	Anhydro-ß-D-glucopyranose (Levoglucosan)	121	324	1060	478	98
57.73	Syringol, 4-(1-Propenyl)- trans	127	114	118	126	121
58.70	Syringaldehyde	41	56	39	41	37
61.92	Coniferyl alcohol trans	115	83	34	36	64
70.93	Sinapaldehyde	58	58	57	58	42

Appendix 3E - Normalised area of pyrolysis products of treated and untreated samples.

			Treated corncob with			
R.T.	Chemical product	Corncob	H_2O	HCl	$CaCl_2$	NaCl
4.51	Acrolein (2-Propenal)	103	138	114	130	121
4.71	Propanal-2-one; Methylglyoxal	307	383	325	397	330
5.97	Butandione, 2,3- (Diacetyl)	97	111	89	93	101
6.39	3-Pentanone	108	81	15	25	81
7.13	Acetaldehyde, hydroxy-	557	556	369	593	603
8.17	Acetic acid	383	361	299	321	378
9.68	Acetol (Hydroxypropanone)	317	246	78	140	311
10.89	Ethene, 1,2-dihydroxy-	11	18	14	18	13
13.71	Ethyleneglycol	9	17	6	39	17
14.38	Propionaldehyde, 3-hydroxy	77	90	70	98	87
15.03	Butenal-2-one, 3-	24	27	8	14	26
15.69	Furanone, 3(2H)	20	28	50	31	22
15.96	Furaldehyde, 3-	10	12	12	17	12
16.59	poss: Oxopropanoic acid methylester, 2-	103	130	28	92	99
16.66	Propanal	170	114	36	37	125
17.36	Furaldehyde, 2-	83	98	209	127	85
19.95	Acetyloxypropane-2-one, 1-	22	21	8	14	21
20.41	Butanone, 2- derivative	23	18	4	6	18
23.01	Cyclopentene-1-one, 2-hydroxy-2-	183	150	64	94	156
24.02	Furan-x-one, x,x-Dihydro-x-methyl-	38	51	48	44	39
24.43	Furaldehyde, 5-methyl-2-	9	12	17	16	10
25.93	Furanone, 2(5H)-	110	115	44	62	104
27.00	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	89	192	348	400	127
27.88	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	56	39	10	25	51
29.78	Phenol	47	33	22	24	41
30.41	Guaiacol	69	51	36	40	63
34.27	5-(Hydroxymethyl)dihydro-2(3H)-furanone	56	56	19	20	43
35.28	Guaiacol, 4-methyl	18	21	26	20	17
41.14	Anhydro-ß-D-arabinofuranose, 1,5-	38	46	117	88	41
41.67	Guaiacol, 4-vinyl-	257	284	250	288	284
41.79	Phenol, 4-vinyl	409	417	302	394	426
43.41	Furaldehyde, 5-(hydroxymethyl)-2-	15	28	93	55	18
43.90	Syringol	47	33	13	14	44
44.99	Furanone, dihydro-4-hydroxy-2(3H)-	15	23	12	18	16
47.32	Anhydro-ß-D-xylofuranose, 1,5-	38	61	264	120	41
47.62	Syringol, 4-methyl	11	13	19	12	11
52.47	Benzaldehyde, 4-hydroxy-	9	10	7	11	10
52.83	Syringol, 4-vinyl	41	33	22	30	41
57.09	Anhydro-ß-D-glucopyranose (Levoglucosan)	75	196	972	418	83
62.55	Coniferyl aldehyde	8	10	18	9	8

Appendix 3E – Ratios of peak areas of catalysed and untreated samples of major volatile products

			Weight normalised peak area ratio					
Assigned no	R.T.	Components	FCC	SN27	MSN	MSM-15	HZSM-5-28	HZSM-5-80
3	5.95	Butandione, 2,3- (Diacetyl)	1.2	1.4	1.1	0.9	1.1	1.7
4	6.40	3-Pentanone	0.6	0.7	0.8	0.3	0.5	0.9
5	7.11	Acetaldehyde, hydroxy-	0.9	0.8	1.0	0.6	0.8	0.6
6	7.92	Butenal-2; Crotonaldehyde trans	1.0	1.6	1.3	0.9	1.0	1.0
7	8.18	Acetic acid	1.0	0.9	0.9	0.9	0.8	0.9
10	9.67	Acetol (Hydroxypropanone)	0.5	0.7	0.7	0.3	0.4	0.5
17	14.41	Propionaldehyde, 3-hydroxy	1.0	1.0	1.0	0.9	0.9	0.9
19	14.95	Furanone, 2(3H)-	1.0	0.9	1.1	0.7	0.7	0.6
20	15.05	Butenal-2-one, 3-	0.7	0.8	0.8	0.2	0.3	0.2
22	15.98	Furaldehyde, 3-	1.6	1.4	1.3	1.6	1.6	2.4
26	17.38	Furaldehyde, 2-	2.4	1.8	1.2	1.6	1.5	4.2
29	21.87	2-Cyclopentene-1,4-dione	1.5	1.5	1.2	1.2	1.3	2.5
31	23.03	Cyclopentene-1-one, 2-hydroxy-2-	0.7	0.7	0.8	0.5	0.6	0.6
32	24.05	Furan-x-one, x,x-Dihydro-x-methyl-	1.3	1.0	1.2	1.1	1.0	0.5
35	25.97	Furanone, 2(5H)-	0.8	1.0	1.2	0.7	0.8	0.7
39	27.04	Pyran-4-one, 3-hydroxy-5,6-Dihydro-(4H)-	1.6	1.6	1.5	2.1	2.0	1.4
40	27.91	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	0.6	0.5	0.6	0.3	0.4	0.3
41	28.15	Pyran-2-one, 3,4-Dihydro-6-methyl-2H-	1.2	1.7	1.5	2.1	2.4	1.4
43	30.44	Guaiacol	1.0	0.9	0.9	1.1	1.1	1.0
51	39.38	unknown carbohydrate	3.7	2.0	2.2	3.9	3.7	3.1
56	41.69	Guaiacol, 4-vinyl-	0.9	0.9	0.9	0.8	0.9	0.9
59	43.94	Syringol	0.9	0.9	0.8	0.8	1.0	0.8
61	45.03	Furanone, dihydro-4-hydroxy-2(3H)-	1.0	0.9	0.9	0.6	0.7	0.5
63	47.30	Guaiacol, 4-propenyl- ; (Isoeugenol) trans	1.4	1.1	1.2	0.7	0.8	1.2
64	47.50	Anhydro-ß-D-xylofuranose, 1,5-	2.2	1.0	1.0	8.3	8.3	2.1
65	47.66	Syringol, 4-methyl	1.4	1.1	1.2	1.5	1.4	1.3
68	48.72	Indene, 6-Hydroxy-7-methoxy-1H-	1.9	1.1	0.9	1.3	1.1	1.9
69	49.12	Indene, 6-Hydroxy-7-methoxy-, 2H-	1.7	1.0	0.9	1.1	1.1	1.5
72	52.87	Syringol, 4-vinyl	0.8	0.9	0.9	0.8	0.8	0.9
73	53.49	Syringol, 4-allyl-	1.0	1.0	1.1	1.1	1.2	1.0
75	56.83	Indene, 6-hydroxy-5,7-dimethoxy-1H-	2.1	1.1	1.1	1.8	1.6	2.7
76	57.17	Anhydro-ß-D-glucopyranose (Levoglucosan)	3.7	1.9	2.1	7.9	6.7	5.7
77	57.76	Syringol, 4-(1-Propenyl)- trans	1.1	1.0	1.1	1.2	1.2	1.0
78	58.74	Syringaldehyde	1.0	1.1	1.1	1.0	1.1	1.0
81	61.07	Acetosyringone	0.9	1.1	1.0	0.8	0.9	0.9

Appendix 4 - Publications

Energy Fuels **2010,** *24,* 2078–2085 · DOI:10.1021/ef9012856
Published on Web 02/04/2010

energy&fuels
article

Fast Pyrolysis of African and European Lignocellulosic Biomasses Using Py-GC/MS and Fluidized Bed Reactor

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Received November 2, 2009. Revised Manuscript Received January 11, 2010

Five biomasses spruce (*Picea abies* L.), beech (*Fagus sylvatica* L.), iroko (*Chlophora excelsa* L.), albizia (*Albizia adianthifolia* L.), and corncob (*Zea mays ssp.*) have been subjected to analytical pyrolysis (Py-GC/MS) and bench-scale pyrolysis with a fluidized bed reactor at 470 °C. The comparison of Py-GC/MS and bench scale results revealed only small differences in the relative concentration of single products mainly acetic acid, hydroxyacetaldehyde, hydroxypropanone, and lignin-derived guaiacyl and syringyl components. For European woods, organic oil yields were approximately 57%, whereas African biomasses yielded between 41 and 48% because of their higher mineral contents. The analysis of bio-oil composition revealed no significant differences between African and European biomasses. Acetic acid, hydroxyacetaldehyde, hydroxypropanone, and levoglucosan were found to be the largest individual components in the volatiles. Bio-oil from corncob, having the lowest lignin content contained high concentration of 4-vinylphenol, a lignin derived product. This implied that the degradation products largely depend on the constituents' structure of the biomass. The higher heating value of all bio-oils ranged 16−17 MJ/kg.

Introduction

The evident global awareness of environmental consequences of petroleum, the major energy source, is promoting the search for renewable energy sources. Consequently, production of renewable fuels from lignocellulosic biomass through various thermochemical conversion processes, namely, pyrolysis, gasification and direct liquefaction have gained prominence in the last three decades.[1−5]

Fast pyrolysis is a rapid heating method employed in converting biomass and organic residues to bio-oil, gas and char.[2] Depending on the operating temperature, pressure and other parameters, such as heating rate and vapor residence time, the quantity of these products in a conversion process can be regulated to favor the desired product.[6,7] Up to 78% of organic rich liquid has been reported between operating temperature of 450 and 600 °C, while temperature above 700 °C principally produces noncondensable gases.[8−10] The organic liquid (bio-oil) is a mixture of hundreds of organic compounds whose exact chemical and physical properties depend on the nature and composition of the original biomass, and the method and condition of production. Generally, bio-oil is a dark brown complex viscous organic and highly oxygenated acidic mixture that is slightly denser than water. Even though its mechanism of formation is not entirely well understood, several researches have been carried out to outline possible reaction mechanisms of formation.[11−13]

Bio-oil has a wide area of applications, as fuels in diesel engines, boilers and turbines, and can equally serve as source of numerous chemicals and polymers. The pyrolysis liquid (bio-oil) can be refined to either improve its quality or to obtain various chemical products.[14,15]

Several investigations have been carried out to determine the parametric influence of temperature, residence time, catalyst, particle size, moisture content, and mineral content on the yield and quality of organic liquid produced.[16−20] Optimal operational parameters however depend on the pyrolysis unit. Fahmi et al.[20] reported the effect of mineral

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(1) Kucuk, M. M.; Demirbas, A. *Energy Convers. Manage*. **1997**, *38*, 151–165.
(2) Bridgwater, A. V. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 3–22.
(3) Demirbas, A. *Energy Convers. Manage*. **2001**, *42*, 1357–1378.
(4) Deng, C. J.; Liu, R. H.; Cai, J. M. *J. Energy Inst*. **2008**, *81*, 211–217.
(5) Mohan, D.; Pittman, C. U.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848–889.
(6) Bridgwater, A. V.; Peacocke, G. V. C. *Renewable Sustainable Energy Rev*. **2000**, *4*, 1–73.
(7) Encinar, J. M.; Beltran, F. J.; Bernalte, A.; Ramiro, A.; Gonzalez, J. F. *Biomass Bioenergy* **1996**, *11*, 397–409.
(8) Scott, D. S.; Majerski, P.; Piskorz, J.; Radlein, D. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 23–37.
(9) Garcia-Perez, M.; Wang, X. S.; Shen, J.; Rhodes, M. J.; Tian, F. J.; Lee, W. J.; Wu, H. W.; Li, C. Z. *Ind. Eng. Chem. Res*. **2008**, *47*, 1846–1854.
(10) Chen, H. P.; Li, B.; Yang, H. P.; Yang, G. L.; Zhang, S. H. *Energy Fuels* **2008**, *22*, 3493–3498.
(11) Liu, Q.; Wang, S. R.; Wang, K. G.; Guo, X. J.; Luo, Z. Y.; Cen, K. F. *Acta Physicochim. Sinica* **2008**, *24*, 1957–1963.
(12) Balat, M. *Energy Sources, Part A* **2008**, *30*, 620–635.
(13) Demirbas, A. *Energy Sources, Part A* **2009**, *31*, 1186–1193.
(14) Czernik, S.; Bridgwater, A. V. *Energy Fuels* **2004**, *18*, 590–598.
(15) Denirbas, A. *Energy Sources* **2004**, *26*, 715–730.
(16) Garcia-Perez, M.; Wang, S.; Shen, J.; Rhodes, M.; Lee, W. J.; Li, C. Z. *Energy Fuels* **2008**, *22*, 2022–2032.
(17) Demirbas, A. *Energy Sources* **2005**, *27*, 823–830.
(18) Dobele, G.; Dizhbite, T.; Rossinskaja, G.; Telysheva, G.; Mier, D.; Radtke, S.; Faix, O. *J. Anal. Appl. Pyrolysis* **2003**, *68−9*, 197–211.
(19) Lee, K. H.; Kang, B. S.; Park, Y. K.; Kim, J. S. *Energy Fuels* **2005**, *19*, 2179–2184.
(20) Fahmi, R.; Bridgwater, A.; Donnison, I.; Yates, N.; Jones, J. M. *Fuel* **2008**, *87*, 1230–1240.

content in biomasses on the quality of bio-oil. It was noted that the ash content of raw materials does not only affect the quantity of char and gas product but equally plays important role in the quality of organic liquid yield. It has been noted that the removal of ash and extractives in pretreatment step prior to pyrolysis substantially improve the quality of bio-oil in terms of molecular weight distribution and homogeneity.[21]

With a yearly average of 30−50% global vegetation burning, Africa is ranked the world largest biomass burning emission source.[22,23] Biomass has been reported to represent 80% of the energetic resources in sub-Sahara Africa.[24] Nigeria with an estimated 9 million hectares of forest area has been reported to have over 80% (about 7 000 000 m^3/annum) woody wastes. The estimation accounted for wastes emanating only from wood logging and sizing operations.[25] Majority of over 2000 saw mills in Nigeria have conversion efficiency less than 60% owing to obsolete milling machines.[26] Wastes generated from these saw mills are considered uneconomical and often set on fire. To sustain the breakthrough in green energy development, Africa with huge agricultural and biomass residue has a vital role to play as a viable source of raw materials.

However, the lignocellulosic composition of biomasses is often affected by the climatic factor and location of plantation. These variations would invariably affect the physical and chemical properties of bio-oil and other byproduct generated from the pyrolysis of these biomasses. Most sub-Sahara Africa plants have high extractives and ash contents due to enormous abundance of soil minerals.[27] To date, little or no effort has been made in the pyrolysis of typical subtropic forestry and agricultural wastes. Therefore, this paper focuses on the fast pyrolysis of different biomasses sourced from sub-Sahara Africa and Europe with a view to compare physicochemical properties of their liquid products using analytical and laboratory scale fast pyrolysis methods.

Methods and Materials

Feedstocks. Five varieties of air-dried biomasses from Europe and sub-Sahara Africa were used as feedstock for the experiments. Beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L.) wood particles were obtained from J. Rettenmaier & Söhne GmbH, Rosenberg, Germany. West African albizia (*Albizia adianthifolia* L.) and iroko (*Chlophora excelsa* L.) sawdust and corncob (*Zea mays ssp.*) were obtained from Omolayo sawmill and Ajebamdele farm settlement, respectively, both located in Ado-Ekiti, Nigeria, where such products are usually burnt off as waste. The materials were ground to size < 1 mm using Retsch cutting mill SM 2000. The resulting samples were sieved through 750, 500, and 300 μm mesh on Retsch sieve shaker model AS 400 for 10 min. Fractions between 300 and 500 μm were collected and stored in sealed polythene bags.

Feedstock Analyses. Physicochemical analyses of the materials were carried out prior to pyrolysis to establish the influence of the biomass constituents on respective products. Moisture contents of all feedstock were gravimetrically determined a day before pyrolysis by drying in an oven at 105 °C for 12 h. Ash contents were determined by heating the samples in a Heraeus furnace at 520 °C for 6 h, cooled in desiccators before weighing. The determination of volatile matter was carried out using a thermogravimetric analyzer (TG 209 F1 Iris, NETZSCH, Germany) in a nitrogen atmosphere. Approximately 10 mg of sample was heated to 700 at 10 °C/min and held for 5 min. Fixed carbon content was then calculated by difference. Samples of all raw materials were successively Soxhlet-extracted using petroleum benzene, followed by acetone and 70% methanol in water. Each extraction step lasted 12 h. Extract-free samples were used for holocellulose and lignin content determinations. The results of proximate and ultimate analyses are depicted in Table 1.

Holocellulose determination was performed using HPAEC-borate. The prehydrolysis step was carried out by digesting 200 mg of milled extract free sample in 2 mL of 72% H_2SO_4 in a thermostat bath at 30 °C. The prehydrolysis was terminated with distilled water after 1 h. Post hydrolysis was carried out at 120 °C under pressure and lasted 50 min using Systec VX-75 autoclave (Systec GmbH, Germany). The hydrolyzed sample was made up to mark in 100 mL standard flask and allowed to stand to cool. This was followed by filtration using 0.45 μm fritted-glass filter. The residue was dried at 105 °C and gravimetrically determined for condensed lignin, while an aliquot of the supernatant was taken for the analysis of various wood sugars on high-performance borate-complex anion-exchange chromatography Ultimate 3000 (Dionex Corp.) equipped with a 6.6 mm Omnifit bore column of 115 mm length. The column is packed with strong anion exchange resin (MCI Gel CA08F (Mitsubishi) at 60 °C). The mobile phase was made of (A) 0.3 M potassium borate buffer pH 9.2 and (B) 0.9 M potassium borate buffer pH 9.2 a gradient elution of 0.7 mlmin^{-1} was used. Separation commenced with 90% A and 10% B, following sample injection with a 35 min linear gradient to 10% A and 90% B. The data acquisition lasted 47 min. Wood sugars were quantified by after-column derivatization with Cu-bichinconinate according to previous authors.[28]

Klason lignin content was estimated as the residue left after sulphuric acid digestion and subsequent hydrolysis of the extract-free sample.[29] Acid soluble lignin was measured on UVIKON 943 UV/vis Spectrometer at 205 nm according to TAPPI 1985b.[30] The value obtained was added to that of the residue to make up reported values.

The inorganic mineral components composition was determined using PerkinElmer ICP-OES (inductively coupled plasma optical emission spectrometry) following the sample acid digestion as follows: Approximately, 100 mg of finely milled sample was digested with 2 mL 70% nitric acid on START 1500 Digestion Microwave (MLS GmbH, Germany). The machine is equipped with a pressure controller, automatic turntable, and closed PFA-line digestion vessels equipped with pressure relief device. The digestion lasted 20 min at 170 °C and 3 bar. The digested sample was then diluted with double distilled water (dilution factor was 50). Prepared samples were measured for Na, Mg, K, Ca. Fe, Mn, Cu, Al, and Zn.

Pyrolysis−GC/MS. Prior to pyrolysis, the samples were milled using HERZOG Pulveriser HSM 100A grinding mill. Approximately, 120 μg of fine-milled sample was weighed in pyrolysis cup and introduced into the pyrolyzer through automatic sampler. Pyrolysis was performed using a double shot

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(21) Das, P.; Ganesh, A.; Wangikar, P. *Biomass Bioenergy* **2004**, *27*, 445–457.

(22) Andreae, M. O. In *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*; Levine, J. S., Ed.; MIT Press: Cambridge, MA, 1991, p 2−21.

(23) Roberts, G.; Wooster, M. J.; Lagoudakis, E. *Biogeosci. Discuss.* **2008**, *5*, 3623–3663.

(24) Guéhenneux, G.; Baussand, P.; Brothier, M.; Poletiko, C.; Boissonnet, G. *Fuel* **2005**, *84*, 733–739.

(25) Dionco-Adetayo, E. A. *Technovation* **2001**, *21*, 55–60.

(26) Aina, O. M. Presented at the International Conference on Renewable Energy for Developing Countries (ICREDC2006), Washington, DC, April 2006.

(27) Fengel, D.; Wegener, G. *Wood: Chemistry, Ultrastructure, Reactions*; Walter de Gruyter & Co.: Berlin, 1984.

(28) Willför, S.; Pranovich, A.; Tamminen, T.; Puls, J.; Laine, C.; Suurnäkki, A.; Saake, B.; Uotila, K.; Simolin, H.; Hemming, J.; Holmbom, B. *Ind. Crops Prod.* **2009**, *29*, 571–580.

(29) Ritter, G. J.; Seborg, R. M.; Mitchell, R. L. *Ind. Eng. Chem., Anal. Ed.* **1932**, *4*, 202–204.

(30) Dence, C. W. The determination of lignin. In *Methods in Lignin Chemistry,* Lin, Y. S.; Dence, W. C., Eds. Springer-Verlag: Berlin, 1992; pp 33−61.

Table 1. Component, Ultimate, and Proximate Analyses of Raw Materials

	component analysis (wt.%)				
	beech	spruce	iroko	albizia	corn cob
extractives	2.4	2.9	8.2	6.2	2.8
Klason lignin	21.8	29.0	26.2	25.2	19.0
holocellulose	68.5	70.2	64.8	63.7	75.7
glucose	46.0	47.4	48.2	45.7	40.4
xylose	18.1	5.8	12.1	14.9	30.9
mannose	1.4	12.9	2.0	1.3	0.1
galactose	1.0	2.3	0.8	0.4	1.0
arabinose	0.5	1.0	0.2	0.2	2.8
rhamnose	0.5	0.2	0.5	0.3	0.1
cellobiose	0.1	0.0	0.0	0.1	0.1
4-*O*-methyl-glucuronic acid	1.0	0.8	0.9	0.9	0.4
	ultimate analysis (moisture and ash free (maf.) wt. %)				
	beech	spruce	iroko	albizia	corn cob
carbon	46.9	48.3	43.9	46.4	43.6
hydrogen	6.2	6.3	5.3	5.8	5.8
nitrogen	0.3	0.4	0.4	0.6	0.7
oxygen[a]	45.9	44.6	46.9	45.5	48.6
HHV MJ/kg[b]	18.7	19.5	16.5	17.4	16.9
	proximate analysis				
ash content mf %	0.7	0.4	3.5	1.8	1.2
moisture content %	9.7	8.4	9.4	9.7	9.7
volatile matter mf %	85.9	83.5	70.4	72.7	80.6
fixed carbon mf %	13.4	16.1	26.1	25.5	18.2

[a] By difference. [b] Calculated according to Boie's equation.

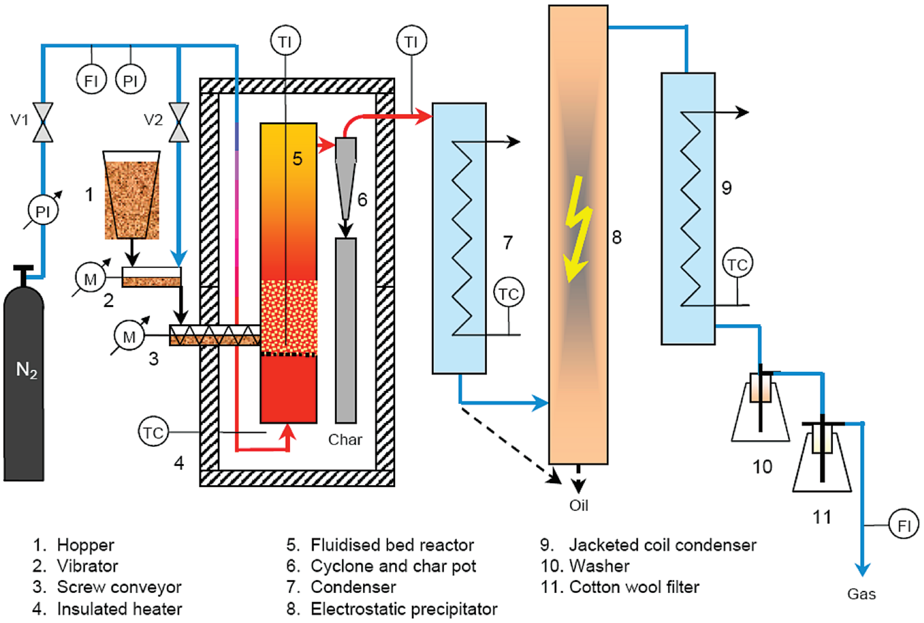

Figure 1. Fluidized bed pyrolysis unit.

Py-2020iD 2020 microfurnace pyrolyzer (Frontier Laboratories Ltd.) mounted on an Agilent 6890 GC system. The machine is equipped with a DB-1701 (Agilent J&W) fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and an Agilent 5973 mass selective detector (EI at 70 eV, ion source temp 280 °C). Pyrolysis was carried out at 470 °C For separation with GC, the oven temperature was held at 45 °C (4 min) and raised to 255 at 3 °C min^{-1} (70 min) using He as carrier gas (1 mL min^{-1}). The compounds were identified using Mass Finder 4 by comparing their mass spectra in NIST and home-developed libraries.

Fluidized-Bed Pyrolysis. A 300 g/h fluidized bed pyrolysis unit at vTI, Hamburg, was employed for the pyrolysis of 250 g feedstock (Figure 1). It consists of a feedstock feeding unit (hopper, vibrator, and screw conveyor), insulated steel reactor (41 mm i.d. and 305 mm height), cyclone with char collector, condenser, electrostatic precipitator (EP), followed by a insulated coil condenser, washer, and cotton wool filter. The condenser (7) was operated with ethanol at 2 °C, the second condenser (9) was fit with a jacket and operated at −30 °C with ethylene glycol, to further obtain condensable organic components from the vapor emerging from the electrostatic precipitator. The reactor was fitted with a temperature and heating control system. The feedstock was continuously fed at about 250 g/h through vibrator agitated hose into vertically positioned silica sand fluidized bed (grain size 300−500 μm). Pyrolysis was carried out at the predetermined optimum pyrolysis

Table 2. Inorganic Constituents of Raw Materials (ppm Dry Basis)

	Na	Mg	K	Ca	Fe	Mn	Cu	Al	Zn
beech	67.7	355.3	1207.8	1683.1	110.8	165.7	0.5	16.7	9.5
spruce	25.9	101.3	380.5	867.2	9.0	176.4	0.0	4.6	11.4
iroko	32.1	790.5	3879.8	8507.3	379.6	26.5	0.5	209.0	8.3
albizia	22.9	171.5	2703.2	3387.8	331.2	9.3	5.1	188.4	5.7
corn cob	29.3	404.7	5408.4	249.3	144.1	9.9	3.9	162.1	58.5

temperature of 465−470 °C and pressure drop of 80 mbar using nitrogen as fluidizing gas. The reactor was preheated to 475 °C prior to the commencement of the pyrolysis after which the temperature was regulated to the desired temperature.

The biomass decomposed in the reactor to form a mixture of vapors and char. The char was separated from the vapor in a cyclone and collected below in a glass flask. The vapors were rapidly quenched in the first condenser (7) and the remaining gas was directed into the EP. The condensates from both the condenser and the EP were combined and collected in a flask to give bio-oil. Further, the gas passed into the jacketed coil condenser to obtain condensable light products. The noncondensable gas was passed into vent. The condensers, reactor sand, EP, and all product collectors were weighed before and after pyrolysis to ensure accurate material balance. Duplicate trials were carried out for each biomass. Mean values of bio-oil, condensate and char yields from all products were calculated and reported in Table 3. The gas yield was calculated by percentage difference.

Bio-oil Analysis. The water content in bio-oils was determined by Karl Fischer method according to ASTM D 1744 using Schott Titro Line alpha. Hydranal Composite 2 (34806) was automatically titrated against Hydranal methanol rapid (37817) supplied by Riedel den Haën, Germany as described by previous authors.[31]

The acidity of the organic products was measured with WTW hand-held meter (pH 3300i). The pH meter has an accuracy of ± 0.003.

The viscosity was determined according to DIN 51562 (part 1 and 2) in an automatic capillary viscosimeter (AVS 350) equipped with a Schott constant temperature bath (CT 1650) The measurement were carried out with U-viscosimeter at 20 and 40 °C.

The elemental analyses of carbon, hydrogen and nitrogen were measured with a CE Instruments CHNS Flash 1112 Analyzer using complete oxidation method. Oxygen was determined by percentage difference. The higher heating values (HHV) of the bio-oil were determined using IKA C2000 basic bomb calorimeter at the laboratory of process engineering, Hamburg University of Applied Sciences according to ASTM D2015.

For the determination of the oil solid content, 3 g of oil was dissolved in 100 mL acetone and the solution was quantitatively filtered through a Whatman nuclepore Track-Etch membrane with a pore size of 0.1 μm. The residual mass was gravimetrically determined.

The precipitation of the pyrolytic lignin (PL) in various bio-oil samples was carried out according to the method of Scholze and Meier.[32] Twenty-five milliliters of deionized water was vigorously agitated using Disperser T 18 Basic Ultra-Turrax at 5000 rpm. Approximately, 250 μL of bio-oil was added in dropwise and the suspension was filtered, thoroughly rinsed and vacuum-dried at 35 °C. The PL fraction was then gravimetrically determined.

The chemical composition of bio-oils was analyzed on Agilent HP 6890 fitted with both FID and HP 5972 MS systems. A weighed amount of oil sample was diluted with acetone (approximately 1:10 on dry basis) including a known amount of fluoranthene used as internal standard. One microliter of the prepared sample was injected (split ratio 15:1) at 250 °C on a 60 m × 0.25 mm Varian Factor Four fused silica column made of 14% cyanopropyl-phenyl-methylpolysiloxane (1701) with film thickness of 0.25 μm. The oven was held at 45 °C for 4 min subsequently raised to 280 °C with heating rate of 4 °C/min and then held for 20 min. The carrier gas was helium with a constant flow of 2 mL min^{-1}. Electron impact mass spectra were obtained using 70 eV ionization energy and an ion source temperature of 280 °C. The analyzed components were identified with Mass Finder 4 by comparing mass spectra and Kovat's indices of components using mass spectra from NIST and home-developed libraries.

Results and Discussion

Characterization of Ligno-cellulosic Raw Materials. The results of raw materials analyses are presented in Table 1. The tropical African woody biomasses were found to be richer in extractives than European woods. These extractives are made up of phenolic compounds, terpenes, aliphatic acids, chinones and alcohols. High content of these components often results in low polyoses content in wood.[27] This is evident in low hemicelluloses contents found in iroko and albizia in comparison to those found in European hard- and softwoods. The analysis of the extractives is beyond the scope of this work.

Spruce has the highest HHV with 19.5 MJ/kg. Corncob was the richest of all samples in terms of hemicelluloses content. In contrast to wood, the high polyoses content in the corncob mainly consist of xylose and arabinose. Xylose and mannose are the main hemicelluloses in beech, iroko, and albizia, while mannose constitutes the main component of hemicelluloses in spruce. The cellulose content estimated from the sugar analysis according to Fengel[27] rough estimation ranged between 40.7 and 47.2%. The overall result largely tallied with earlier findings on the chemical composition of these ligno-cellulose.[27,33]

Result of the inorganic components in all samples in Table 2 indicates that the three selected African samples were found to be considerably richer in potassium and calcium than the two other European samples. These metals constitute the main inorganic component in all samples.

Bio-oil Production. The operational conditions for duplicate trials of each of the five raw materials were fairly constant with relatively similar feedstock feeding rate and pyrolysis temperature between 465 and 470 °C. This temperature range had been found optimal for most biomasses previously pyrolyzed in the reactor.[34,35] Each pyrolysis experiment lasted approximately 60 min in order to obtain sufficient homogeneous products. The minimum parametric difference manifested no significance in the results.

Two liquid streams were collected from the pyrolysis namely, bio-oil from condenser/EP (7, 8) and condensate

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(31) Oasmaa, A.; Meier, D. *J. Anal. Appl. Pyrolysis* **2005**, *73*, 323–334.

(32) Scholze, B.; Meier, D. *J. Anal. Appl. Pyrolysis* **2001**, *60*, 41–54.

(33) Donnelly, B. J.; Helm, J. L.; Lee, H. A. *Cereal Chem.* **1973**, *50*, 548–552.

(34) Bayerbach, R.; Nguyen, V. D.; Schurr, U.; Meier, D. *J. Anal. Appl. Pyrolysis* **2006**, *77*, 95–101.

(35) Bayerbach, R.; Meier, D. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 98–107.

Table 3. Mass Balance of the Fast Pyrolysis of Biomasses[a]

	beech	spruce	iroko	albizia	corn cob
reactor temperature	465−470 °C	465−470 °C	465−470 °C	465−470 °C	465−470 °C
total liquid product wt %	70.1	69.9	56.4	61.4	61.3
bio oil wt %	62.7	62.7	50.6	54.7	56.2
condensate wt %	7.4	7.3	5.8	6.7	5.1
organic[b]mf wt %	57.5	57.1	40.4	47.6	43.9
gas[c]	22.6	23.0	23.1	24.3	27.2
char daf %	10.2	10.1	22.8	16.6	14.7
pyrolytic water wt %	9.7	9.8	13.3	11.2	14.0
biomass-to-volatiles wt %	88.7	86.7	77.5	83.3	83.6

[a] Mean values of duplicate pyrolysis trials. [b] Organic = bio-oil + condensate − (water content of bio oil + water content of condensate). [c] Percentage by difference based on wet weight.

Table 4. Physicochemical Analyses of Bio-oil, Condensate, and Char

	beech	spruce	iroko	albizia	corn cob
		bio-oil			
water content %	22.2	22.0	32.3	25.1	32.2
viscosity (40 °C) cST	15.2	14.8	-	57.1	6.7
pH	2.5	2.8	2.9	2.9	3.0
solid content %	0.2	0.1	0.2	0.2	0.1
lignin content %	15.0	15.4	14.1	12.2	8.5
carbon %	41.4	42.3	38.2	41.9	38.1
oxygen %[a]	51.2	50.3	54.0	50.1	53.2
hydrogen %	7.1	7.2	7.5	7.4	8.0
nitrogen %	0.2	0.2	0.3	0.6	0.7
HHV MJ/kg	16.9	17.2	15.9	17.4	15.8
carbon mf. wt%	53.3	54.2	56.5	55.9	56.2
oxygen mf. wt%	20.7	19.8	8.5	14.9	7.7
hydrogen mf. wt%	6.0	6.1	5.8	6.2	6.6
nitrogen mf. wt%	0.3	0.3	0.4	0.8	1.0
HHV MJ/kg[b]	23.4	24.0	25.6	25.2	25.6
		condensate			
water content	64.2	66.3	76.6	70.4	74.3
carbon mf wt. %	40.4	44.51	46.0	37.2	42.7
		char (maf wt. %)			
carbon	73.6	72.9	68.4	70.4	67.7
oxygen[a]	6.3	12.8	15.3	15.8	9.2
hydrogen	3.4	3.3	3.4	3.1	3.2
nitrogen	0.2	0.2	0.2	0.4	0.5
HHV MJ/kg[b]	29.1	28.0	26.3	26.6	26.5

[a] By difference. [b] Values calculated according to Boie's equation.

from second condenser (9). Mass balance was established to evaluate the performance of the pyrolysis unit. Individual hardware components of the pyrolysis unit were weighed before and after each trial. The adhered oil and trapped char in condensers were removed with ethanol. Each fraction was gravimetrically determined and subsequently added to main products. The results of mass balance (by weight) are presented in Table 3. Mean values of duplicate trials are reported. The total liquid products from the raw material ranged 61−70%. The results revealed an inverse relationship between liquid yield and ash content in pyrolysis as noted by previous authors.[20] Beech and spruce exhibit the highest conversion with 88.7 and 86.7 wt. % respectively. They both had approximately 70 wt. % total liquid product with moderate char (10%) and noncondensable gases (~23%). Iroko has the least organic and highest char yield with 40.4 and 22.8 wt. % respectively.

Pyrolytic water (PW) represents the additional water fraction resulting mainly from dehyadration of the polyoses. PW was estimated by subtracting the moisture content of the raw material from the water content of the whole liquid product. Corncob yielded the highest amount of PW (14 wt %) possibly because of its very high content of polyoses compared to other feedstocks (see Table 1).

Characterization of Bio-oil. The results of various physicochemical analyses are presented in Table 4. Water contents of all samples were similarly related to their PW contents with 22% and 32.3% found in spruce and iroko respectively. In terms of elemental analysis, results revealed that all the biomasses produced similar bio-oil quality. Bio-oils are known to be highly oxygenated liquids. Spruce and albizia were found richest in carbon content (~42%) as similarly explicated by their higher heating values, indicating an improvement in all bio-oil over their respective raw material excluding the water content. Bio-oils obtained from all biomass gave a one-phase liquid but iroko contained slightly higher polymeric constituents probably owing to the nature of its lignin structure or extractive content (see Table 1), which impaired an accurate determination of its viscosity.

GC/MS of Bio-oil. GC/MS was employed to identify and quantify the GC-detectable compounds in the bio-oils. Approximately 75% of the peak total area in each chromatogram, neglecting the solvent peak, was identified and quantified. The quantified fraction, representing 33−44 wt. % dry basis of the whole bio-oil, was categorized into major chemical classes namely: acids, nonaromatic aldehydes, nonaromatic ketones, furans, pyrans, sugars, benzenes, catechols, lignin derived phenols, guaiacols and syringols. The residual fraction consists of water and oligomeric fractions from decomposed carbohydrates and pyrolytic lignin that can not be quantified with GC/MS.[32,35] A summary of the analyses is presented in Table 5 and Figure 2. The values reported are mean values from duplicate analyses. Acetic acid, hydroxyacetaldehyde and hydroxypropanone were detected with highest concentrations in all products. Bio oil from corncob was found to have the highest yield of hydroxypropane and most acidic. This observation can be directly related to the amount of xylose present in corncob. The acidity of corncob bio oil measured with pH meter was slightly lower compared to others (see Table 4) owing to the dilution caused by high volume of pyrolytic water in the corncob bio oil, thereby reducing the hydrogen ion concentration.

Xylose is the most abundant hemicellulose found in hardwood and one year plants. Its degradation during pyrolysis is known to result in the production of acetic and propionic acids, methanol, water, hydroxyl-1-propanone, hydroxyl-1-butanone, and 2-furfuraldehyde.[5,36] The proportions of these components in bio-oils largely reflect their hemicelluloses contents. Acetic acid is formed from the elimination of acetyl groups in 4-methyl-3-acetyl-glucuronoxylan while water results from dehydration reaction of the polyoses.

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(36) Balat, M. *Energy Sources, Part A* **2008**, *30*, 649–659.

Table 5. GC-Detectable Components in Bio-oils

		weight percent (dry basis)				
	components	beech	spruce	iroko	albizia	corn cob
	acids	**8.2**	**2.6**	**6.7**	**7.1**	**9.1**
1.	acetic acid	8.0	2.5	6.1	6.8	8.5
2.	propionic acid	0.2	0.1	0.6	0.3	0.6
	nonaromatic aldehydes	**10.3**	**11.3**	**9.1**	**9.1**	**7.3**
3.	acetaldehyde, hydroxy-	7.9	9.8	7.0	6.7	5.1
4.	propionaldehyde, 3-hydroxy	1.4	0.9	0.8	1.0	0.9
5.	butandial or propanal	1.0	0.6	1.3	1.4	1.4
	nonaromatic ketones	**5.1**	**4.2**	**8.1**	**5.8**	**10.2**
6.	acetol (hydroxypropanone)	2.7	2.4	4.3	3.1	4.7
7.	butanone, 1-hydroxy-2-	0.3	0.2	0.6	0.4	1.3
8.	acetoin; hydroxy-2-butanone, 3-	0.1	0.1	0.1		
9.	propanone, acetyloxy-2-	0.1	0.1	0.1	0.1	0.3
10.	cyclopentene-1-one, 2-	0.2	0.1	0.3	0.2	0.4
11.	cyclopentene-1-one, 2,3-dimethyl-2-			< 0.0		0.1
12.	cyclopentene-1-one, 2-methyl-2-	< 0.0	< 0.0	0.1	0.1	0.2
13.	cyclopentene-1-one, 3-methyl-2-	< 0.0	< 0.0	0.1	< 0.0	0.1
14.	cyclopentene-1-one, 2-hydroxy-2-	1.2	0.9	1.4	1.2	1.9
15.	cyclopentene-3-one, 2-hydroxy-1-methyl-1-	0.5	0.3	1.1	0.6	1.3
	furans	**2.4**	**2.5**	**2.8**	**2.7**	**3.3**
16.	furanone, 2(5H)-	0.6	0.5	0.7	0.6	0.6
17.	furaldehyde, 2-	0.6	0.4	0.5	0.6	1.0
18.	furaldehyde, 3-					0.1
19.	furaldehyde, 5-methyl-2-		0.1	0.1	0.1	0.1
20.	furaldehyde, 5-(hydroxymethyl)-, 2-		0.3			
21.	furan-2-one, 5-methyl-, (5*H*)-	0.1	< 0.0	0.1	0.1	0.1
22.	furan-2-one, 3-methyl-, (5*H*)-	0.1	0.1	0.1	0.1	
23.	furan-*x*-on, *x*,*x*-dihydro-*x*-methyl-	0.3	0.2	0.2	0.2	0.2
24.	butyrolactone, γ-	0.1	0.1	0.2	0.2	0.2
25.	butyrolactone, 2-hydroxy-, γ-	0.3	0.4	0.5	0.4	0.5
26.	furan-2-one, 4-methyl-(5*H*)-	0.1	0.1	0.1	0.1	0.1
27.	lactone derivative	0.3	0.3	0.3	0.5	0.4
28.	lactone derivative		0.1			0.1
	pyrans	**1.9**	**1.8**	**0.7**	**1.2**	**1.3**
29.	maltol (pyran-4-one, 3-hydroxy-2-methyl-4*H*-)			0.2	0.1	0.3
30.	pyran-4-one, 3-hydroxy-5,6-dihydro-, (4*H*)-	1.5	0.9	0.5	1.0	0.9
31.	pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4*H*)-	0.3	0.9	0.1	0.1	0.1
	sugars	**3.3**	**5.3**	**2.3**	**2.6**	**3.4**
32.	anhydro-β-D-arabinofuranose, 1,5-					0.4
33.	anhydro-β-D-xylofuranose, 1,5-	0.2				0.6
34.	anhydro-β-D-glucopyranose, 1,6- (levoglucosan)	2.4	4.5	1.1	1.4	1.2
35.	dianhydro-α-D-glucopyranose, 1,4:3,6-	0.2	0.1	0.3	0.2	0.4
36.	anhydrosugar unknown	0.5	0.8	1.0	0.5	0.9
	benzenes	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
37.	toluene	0.1	0.1	0.1	0.1	0.1
	catechols	**< 0.0**	**< 0.0**	**0.4**	**0.1**	**0.3**
38.	hydroquinone (benzene, 1,4-dihydroxy-)	< 0.0		0.3	0.1	0.2
39.	benzenediol, methyl-			0.1	0.1	0.1
	lignin-derived phenols	**0.2**	0.4	**0.9**	**0.4**	**3.6**
40.	phenol	< 0.0	0.1	0.2	0.1	0.3
41.	cresol, *o*-	< 0.0	0.1	0.1	< 0.0	0.1
42.	cresol, *p*-	< 0.0	< 0.0	0.1	< 0.0	0.1
43.	cresol, *m*-	< 0.0	< 0.0	0.1	< 0.0	0.1
44.	phenol, 2,4-dimethyl-	0.1	0.1	0.1	0.1	< 0.0
45.	phenol, 4-ethyl-			< 0.0	< 0.0	0.3
46.	phenol, ethyl-methyl-					< 0.0
47.	phenol, 4-vinyl-			0.3	< 0.0	2.5
48.	benzaldehyde, 4-hydroxy-					0.1
49.	benzaldehyde, hydroxy-	0.1	0.1	0.1	0.1	0.1
	guaiacols (methoxy phenols)	**1.4**	**4.0**	**4.0**	**2.7**	**3.5**
50.	guaiacol	0.2	0.4	0.8	0.5	0.5
51.	guaiacol, 4-methyl-	0.1	0.4	0.3	0.2	0.2
52.	guaiacol, 4-ethyl-	< 0.0	0.1	0.1	0.1	0.2
53.	guaiacol, 4-vinyl-	0.1	0.4	0.7	0.4	1.7
54.	guaiacol, 4-allyl- (eugenol)	0.1	0.2	0.1	0.1	0.1
55.	guaiacol, 4-propyl-		< 0.0	< 0.0	< 0.0	< 0.0
56.	guaiacol, 4-propenyl-*cis* (isoeugenol)	0.2	0.3	0.3	0.2	0.1
57.	guaiacol, 4-propenyl-(*trans*) (isoeugenol)	0.2	0.5	0.6	0.4	0.2
58.	vanillin	0.2	0.5	0.3	0.2	0.3
59.	phenylacetaldehyde, 4-hydroxy-3-methoxy- (homovanillin)	0.1	0.3	0.2	0.1	
60.	dihydroconiferyl alcohol		0.1			
61.	coniferyl alcohol, isomer of		0.2	0.1	0.1	
62.	phenylethanone, 4-hydroxy-3-methoxy- (acetoguaiacone)	0.1	0.3	0.3	0.2	0.1

Table 5. Continued

components		weight percent (dry basis)				
		beech	spruce	iroko	albizia	corn cob
63.	propioguaiacone		0.1			
64.	guaiacyl acetone	< 0.0	0.1	0.1	< 0.0	0.1
65.	coniferylaldehyde	0.1	0.2	0.2	0.2	< 0.0
	syringols (dimethoxy phenols)	**3.0**	**< 0.0**	**3.0**	**3.3**	**1.2**
66.	syringol	0.5		0.7	0.6	0.3
67.	syringol, 4-methyl-	0.2		0.2	0.2	0.1
68.	syringol, 4-ethyl-	0.1		0.1	0.1	< 0.0
69.	syringol, 4-vinyl-	0.3		0.5	0.5	0.2
70.	syringol, 4-allyl-	0.1		0.2	0.1	0.1
71.	syringol, 4-propyl-	0.1		0.1	0.1	
72.	syringol, 4-(1-propenyl)-, *cis*	0.1		0.1	0.1	0.1
73.	syringol, 4-(1-propenyl)-, *trans*	0.3		0.3	0.4	0.2
74.	syringaldehyde	0.3		0.2	0.3	< 0.0
75.	homosyringaldehyde	0.1		0.1	0.1	
76.	sinapyl alcohol, isomer of	0.1			0.1	
77.	acetosyringone	0.2		0.2	0.2	0.1
78.	propiosyringone	0.1			0.1	< 0.0
79.	syringylacetone	0.1		0.1	0.1	< 0.0
80.	sinapaldehyde (*trans*)	0.5		0.3	0.5	
	total	**36.3**	**32.7**	**38.7**	**35.7**	**44.0**

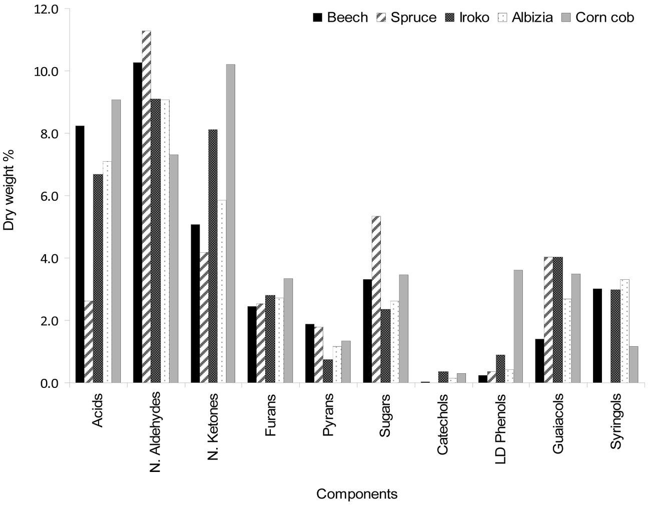

Figure 2. GC/MS detectable chemical classes in bio oil.

Bio-oil obtained from spruce was found to contain the highest amount of hydroxyacetaldehyde and levoglucosan which ranged between 7 and 11% and 1.2−4.5% (dry weight), respectively. Both are main degradation products formed from cellulose during pyrolysis and bio-oil can contain up to 13 wt % of the former.[37,38] Noticeably, the highest concentrations of these substances were however not found in iroko, the richest in glucose content. High content of potassium and calcium found in African biomasses is suspected to be responsible for this disparity. These metals induce glucose fragmentation rather than the depolymerisation of the cellulose polymer that predominates in their absence. They also cause high char and low organic yield especially, levoglucosan in pyrolysis.[39,40]

Levoglucosan, the most important primary degradation product of cellulose is formed from the depolymerization reaction through transglycosylation which occurs at temperature around 300 °C. Its further transformation through fission and disproportionation ultimately leads to the formation of furan and acids.[41] The result revealed that cleavage of various hemicelluloses unit from their respective polysaccharides (depolymerisation) precedes degradation reactions. As indicated in Table 1, the sum of glucose from cellulose and hemicelluloses in spruce is higher compared to similar content in hardwood, hence, the largest quantity of levoglucosan in the softwood. 1,4:3,6-Dianhydro-α-D-glucopyranose, another significant sugar product in the obtained bio-oils, is a dehydrated form of levoglucosan.

A large concentration of 4-vinyl-phenol was only found in corncob bio-oil. This effect is related to the *p*-coumaryl alcohol forms lignin found in one-year plants, whose degradation probably produced the product. Similarly, this product could have resulted from the degradation of ferulic acid; a precursor in the manufacture of many aromatic compounds in plant cell walls, which is largely found within the lignin matrix of corncob.[42] It is can be deducted that the lignin found in many plant is probably formed through different pathways. Although no dimethoxy-phenol and related products were detected in spruce wood the results depicted in Table 5 indicated that highest concentration of monomethoxy-phenols such as vanillin, isoeugenol, guaiacol, etc., was found in spruce, the biomass with highest lignin content. Albizia had the highest yield of dimethoxy fractions, which include syringol, 4-(1-propenyl)-trans syringol, and sinapaldehyde with 3.3 wt %. Two catechols, namely, hydroquinone and methylbenzenediol (0.1−0.3 wt. %) were other lignin-derived products detected only in the African biomasses.

The result of GC/MS analysis of condensates (from condenser 9, Figure 1) is depicted in Figure 3. The result revealed that this fraction was 2−3 times richer in volatile compounds comprising nonaromatic alcohols, aldehydes, ketones, methanol, hydroxyacetaldehyde, hydroxypropane, and 2-furaldehyde than the bio-oil. Concentrations of acetic

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(37) Shafizadeh, F. *J. Anal. Appl. Pyrolysis* **1982**, *3*, 283–305.

(38) Mullen, C. A.; Boateng, A. A. *Energy Fuels* **2008**, *22*, 2104–2109.

(39) Dobele, G.; Rossinskaja, G.; Diazbite, T.; Telysheva, G.; Meier, D.; Faix, O. *J. Anal. Appl. Pyrolysis* **2005**, *74*, 401–405.

(40) Richards, G. N.; Zheng, G. C. *J. Anal. Appl. Pyrolysis* **1991**, *21*, 133–146.

(41) Aho, A.; Kumar, N.; Eranen, K.; Holmbom, B.; Hupa, M.; Salmi, T.; Murzin, D. Y. *Int. J. Mol. Sci.* **2008**, *9*, 1665–1675.

(42) Galletti, G. C.; Reeves, J. B.; Bocchini, P.; Muscarella, C. I. *J. Agric. Food Chem.* **1997**, *45*, 1715–1719.

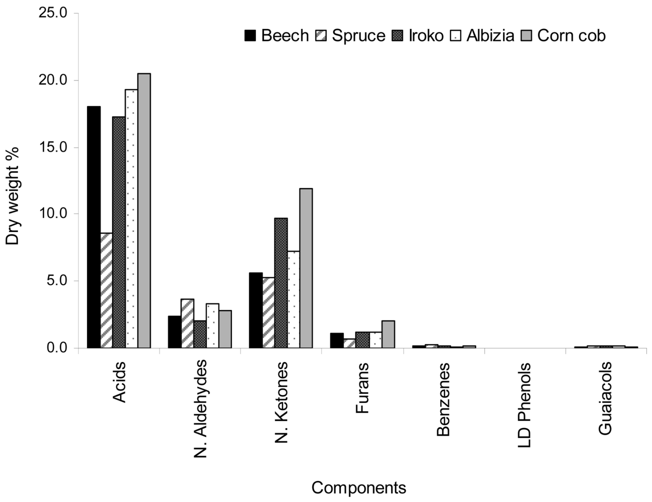

Figure 3. GC/MS detectable chemical classes in condensate.

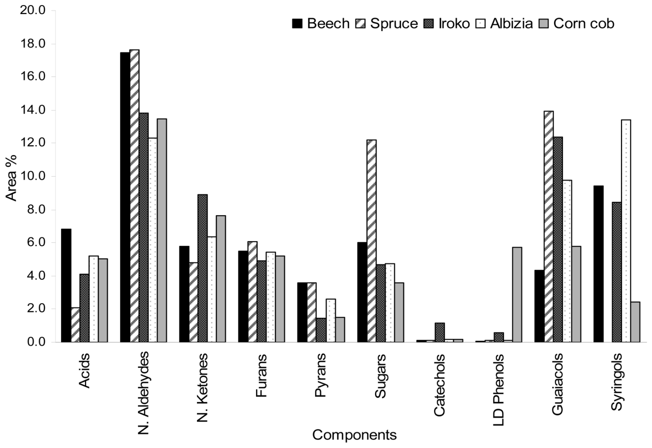

Figure 4. Chemical classes from PY-GC/MS experiments.

and propionic acids were even found to be up to 4 times higher in the condensate. For chemical production, this aqueous fraction would be desirable. In addition, the acidity of pyrolysis oil can be reduced by careful control of pyrolysis condensation temperatures.

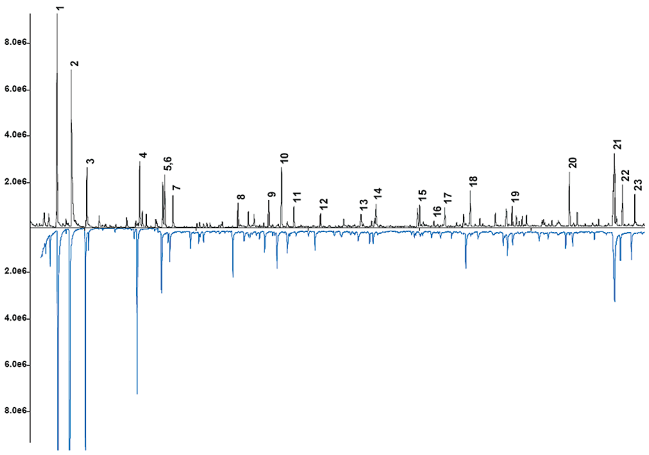

Figure 5. Overlay of GC/MS chromatograms obtained from bio-oil (below) and PY-GC/MS of beech: **1**, acetaldehyde, hydroxy-; **2**, acetic acid; **3**, acetol (hydroxypropanone); **4**, propionaldehyde, 3-hydroxy; **5**, prob. oxopropanoic acid methylester; **6**, butandial; **7**, furaldehyde, 2-; **8**, cyclopentene-1-one, 2-hydroxy-2-; **9**, furanone, 2(5*H*)-; **10**, pyran-4-one, 3-hydroxy-5,6-dihydro-(4*H*)-; **11**, cyclopenten-1-one, 2-hydroxy-3-methyl-2-; **12**, guaiacol; **13**, (*S*)-(+)-2′,3′-dideoxyribonolactone; **14**, guaiacol, 4-methyl; **15**, furanone, dihydro-4-hydroxy-2(3*H*)-; **16**, dianhydro-mannopyranose, 1,4:3,6-; **17**, guaiacol, 4-vinyl-; **18**, syringol; **19**, syringol, 4-methyl; **20**, syringol, 4-vinyl; **21**, anhydro-ss-D-glucopyranose (levoglucosan); **22**, syringol, 4-(1-propenyl)-*trans*; **23**, syringaldehyde.

Pyrolysis-GC/MS. The result of analytical pyrolysis carried out is presented in Figure 4. A duplicate pyrolysis was conducted for each raw material and the mean values of peak area % were reported. In comparison to the bio-oils obtained in the fluidized-bed reactor, smaller fractions of acids and nonaromatic aldehydes and ketones were observed. In addition, higher concentrations of guaiacols and syringols representing 4−14 and 2−14 peak area %, respectively, were found. Differences noted in the guaiacols and syringols fractions from both pyrolysis units can be related to units' configuration. For example the analytical pyrolysis unit is air-tighter; capable of promoting the cleavage of α- and *β*-aryl-alkyl-ether linkages in lignin constituents more effectively thereby enhancing the degradation of lignin with higher conversion that produces lesser charcoal than in fluidized bed. The comparison of chromatograms obtained from the GC/MS of bio-oil and corresponding PY-GC/MS (see Figure 5) indicates no significant differences in the quality but in the relative proportion of pyrolysis products.

Conclusions

This work has demonstrated the practicability of converting lignocellulosic agricultural wastes from sub-Saharan Africa to bio-oil, which, in terms of quality, compared favorably with similar liquid products (bio-oils) obtained from European biomasses. The results revealed that the pyrolysis of African hardwood biomasses resulted in lower organic yield, but high pyrolytic water and char contents compared to European biomasses. High content of monovalent potassium and divalent calcium in African biomasses appeared to have promoted dehydration of holocellulose and demethoxylation of lignin unit following pyrolysis. This effect has resulted in the production of high pyrolytic water and char contents and more catechols and phenols in their bio oils. Pretreatment of African biomasses through washing to remove the ash content is an option that may be adopted to improve the organic yield of these lignocellulosic materials. The close agreement observed in the composition of the volatile pyrolysis products from Py-GC/MS and bench-scale pyrolysis makes the former a reliable online technique for qualifying pyrolysis products and offers potential for the study of their mechanisms of formation.

Acknowledgment. The authors appreciate the financial assistance rendered by German Academic Exchange Service (DAAD) for awarding PhD scholarship to Mr. Azeez. We equally thank the workers in the wood chemistry technology unit of the Johann Heinrich von Thünen-Institute, (vTI, Hamburg) especially Mrs. I. Fortmann for her technical assistance.

Journal of Analytical and Applied Pyrolysis 90 (2011) 81–92

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Review

Temperature dependence of fast pyrolysis volatile products from European and African biomasses

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ARTICLE INFO

Article history:
Received 22 June 2010
Accepted 24 November 2010
Available online 10 December 2010

Keywords:
Volatile products
Pyrolysate
Lignin
Holocellulose
Levoglucosan
Analytical pyrolysis
Fragmentation

ABSTRACT

Chemical composition of two European woods: spruce (*Picea abies* L.), beech (*Fagus sylvatica* L.) and three African biomass residues: iroko (*Chlophora excelsa* L.), albizia (*Albizia adianthifolia* L.), and corncob (*Zea mays* ssp.) have been studied at temperatures between 300 and 700 °C using an analytical pyrolysis unit. The relative amounts of volatile products in individual biomass were largely influenced by pyrolysis temperature and metal content. Most condensable volatile products attained maximum yield between 450 °C and 500 °C. Nearly all lignin derived compounds decomposed to low molecular aromatic compounds at high temperature (650–700 °C) due to severe fragmentation of the aryl substituent. Improved yields in aromatic products observed at high temperatures are related to lignin units of individual biomass. The removal of exchangeable ions in the biomasses resulted in predominance of depolymerisation and dehydration reactions as favoured decomposition pathways for holocellulose. This is exemplified by the reduction in yields of holocellulose-derived low molecular products and enhancement in the formation of anhydrosugars and high molecular furan and pyran products. However, no preferential improvement in the yield of affected volatile products was observed in African biomasses compared to European biomasses as expected following the removal of the ions by the use of diluted acid and distilled water.

Contents

1. Introduction

The search for alternative energy source has taken the centre stage in the last decade, in view of environmental problems associated with over dependence on petroleum. Among solutions so far proffered is the use of biomass with net carbon emission of zero for fuel purpose and as raw material for generating green chemicals [1,2]. Fast pyrolysis is an effective method of converting biomass in the absence of air to produce condensable volatiles, char and mixtures of non-condensable gases. It has gained prominence as a promising alternative means of producing energy and chemicals though not without limitations [3,4]. Renewable energy experts are

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doi:10.1016/j.jaap.2010.11.005

still facing some challenges in their bid to effectively replace hydrocarbon fuels with organic liquids from biomass [5]. These arise from lack of acumen of the conversion chemistry owing to its complexity [6,7]. Meanwhile, to effectively study the viability of lignocelluloses as a source of chemical production, we need good understanding of the behaviour of various lignocelluloses under various pyrolytic operating conditions such as temperature, heating rate, residence time as well as the contributions of indigenous metal ions to the emerging chemical species. This would in a way give us the insight on how to optimise desired pyrolysates. It has been noted that the distribution of chemical species in the complex mixture depends on the nature of the biomass and the pyrolytic conditions [8].

Studies on effects of temperature on pyrolysis products from different lignocellulosic biomasses have been carried out with a view to evaluate overall yields and chemical species in their products through different thermo-chemical conversion methods [9–11]. The optimum yield of condensable products has been found between 400 and 550 °C owing to effective degradation of both polysaccharides and lignin moiety at high temperature [11]. Main components of biomass exhibit different thermal behaviours. For instance, hemicelluloses and cellulose decompose at temperatures between 220–315 °C and 300–500 °C, respectively. The lower thermal stability of hemicelluloses has been attributed to xylose and arabinose contents which are more prone to hydrolysis and dehydration reaction than the hexoses [12]. The decomposition of holocellulose begins with dehydration and condensation reactions, leading to the formation of water, weak acids CO, CO_2 and numerous organic products at low temperature. Fragmentation and rearrangement reactions predominate at high temperature ranges [13]. Shafizadeh and Fu [13] have noted that pyrolysis at temperature above 350 °C induces the cleavage of glycosidic bonds in cellulose. The depolymerisation process is followed by anhydrosugar formation through transglycosylation. Even though lignin is known to be thermally stable, it begins to undergo exothermic decomposition at temperature as low as 200 °C and the thermal degradation continues up to 900 °C [14]. The pyrolysis of individual wood components has helped in explaining their thermal behaviour. However, the thermo-chemical behaviour of biomass during the pyrolysis cannot be summed entirely as aggregate of individual major components because of synergetic effect among different components and other factor such as the degree of polymerisation of cellulose [15,16].

Indigenous metal ions in wood play significant roles in the formation of volatile compounds during the pyrolysis of biomass [17]. They promote the formation of char, water and gases at the expense of condensable organic products during pyrolysis [18]. Their removal alters the mechanism of formation of volatiles among all major components of wood [19]. A high yield of anhydrosugars has been reported in the volatile product composition following the removal of indigenous metal ions in biomass [20]. However, Kleen and Gellerstedt [19] noted in their work that the nature of the metal ion plays an important role. While calcium ion promotes the formation of anhydrosugar, sodium on the other hand suppresses the transglycosylation reaction and promotes demethoxylation and dehydration reactions in lignocellulosic materials.

As previously mentioned, the effects of temperature and metal ions on pyrolysis yields of various biomasses are well documented. However, there are scanty reports on how the temperature affects the production of individual chemical species in condensable organic products obtained from fast pyrolysis. Also, variations in the physicochemical properties of biomasses based on their origin have been noted to influence their pyrolytic products [21]. Therefore, this work is committed to elucidating the role of temperature and the influence of biomass type on the chemical composition of pyrolysis volatile products.

Table 1
Components analysis of raw materials.

	Component analysis (wt.%)				
	Beech	Spruce	Iroko	Albizia	Corn cob
Extractives	2.4	2.9	8.2	6.2	2.8
Klason lignin	21.8	29.0	26.2	25.2	19.0
Holocellulose	68.5	70.2	64.8	63.7	75.7
Glucose	46.0	47.4	48.2	45.7	40.4
Xylose	18.1	5.8	12.1	14.9	30.9
Mannose	1.4	12.9	2.0	1.3	0.1
Galactose	1.0	2.3	0.8	0.4	1.0
Arabinose	0.5	1.0	0.2	0.2	2.8
Others	1.6	1.0	1.4	1.3	0.6
Glucose	46.0	47.4	48.2	45.7	40.4

Azeez et al. [21].

2. Methods and materials

2.1. Feedstocks

Five varieties of biomasses from Europe and Sub-Sahara Africa were selected for the experiment namely; beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L.) wood particles (obtained from J. Rettenmaier & Söhne GmbH, Rosenberg, Germany), West African albizia (*Albizia adianthifolia)* and iroko (*Chlophora excelsa*) sawdust and corncob (*Zea mays* ssp.) which were respectively obtained from Omolayo sawmill and Ajebamidele farm settlement both in Ado-Ekiti, Nigeria. Prior to analysis and pyrolysis, the samples were milled using HERZOG Pulveriser HSM 100A grinding mill. Chemical composition of feedstock as carried out by Azeez et al. [21] is depicted in Table 1.

2.2. Sample washing

Approximately 50 mg of milled sample was weighed into centrifuge micro-tubes (Eppendorf) and 1 ml of washing solution (distilled water or 0.1 M HCl) was introduced. The mixture was allowed to stand for 15 min with intermittent vigorous shaking using test tube shaker. The supernatant was gently decanted following 10 min centrifugation in a Sorvall RC-5C Plus Superspeed Centrifuge at 10,000 rpm and 20 °C. The sample was then rinsed with 1 ml of distilled water using the same procedure outlined above. The treated samples and untreated samples were dried over P_2O_5 in a vacuum-oven at 30 °C for 6 h.

2.3. Pyrolysis – GC/MS

Approximately 80 μg of fine-milled sample was weighed in pyrolysis cup and introduced into Py-2020iD micro-furnace pyrolyzer (Frontier Laboratories Ltd.). The pyrolyzer was mounted on an Agilent 6890 GC system. Pyrolysis of samples was carried out at temperatures between 300 °C and 700 °C with an interval of 50 °C. The cup fell into the preheated furnace set at the desired temperature and the sample was rapidly pyrolysed within 12 s. The pyrolysis vapour was flushed with helium gas into the GC. The GC is fitted with a DB-1701 (Agilent J&W) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thicknesses), flame ionization detector and an Agilent 5973 mass selective detector (EI at 70 eV, ion source temperature 280 °C). For effective separation of the components, the oven temperature was held at 45 °C (4 min) and raised to 255 °C at 3 °C min^{-1} (70 min) using He as carrier gas (1 ml min^{-1}). A duplicate trial was carried out for each analysis. With few discrepancies among components with low yield, duplicate values showed high reproducibility with relative standard deviations ranging between 0.3 and 10% for the most identified components. Mean values of

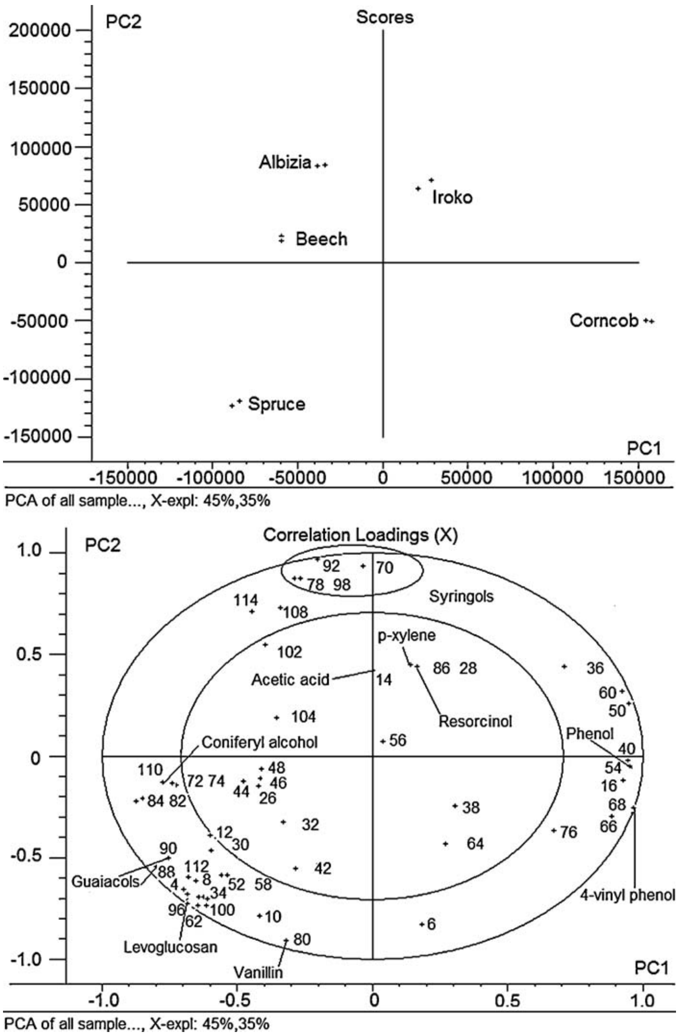

Fig. 1. PCA scores and correlation loadings of Py-GC/MS data from five different lignocellulosic samples.

duplicate peak areas were obtained and used for the evaluation.

2.4. Data treatment

Volatile components were identified using Mass Finder 4 by matching their mass spectra with those in NIST and home-developed libraries. MS signals were only used for identification and the peak areas in FID signal were used for quantification. Each peak area was normalised by the amount of sample used. All samples at 500 °C were also quantified using home developed MS-SIM Tools (MS SIM 1.0.4). This tool enables efficient single ion quantification of many components up to 50 multiple chromatographic measurements in a single evaluation step. Unscrambler 8.0 was used for the principal component analysis (PCA). This statistical tool offers a reliable means of estimating the similarities and dissimilarities in pyrolysis products from different biomass. Differences arising from the compositional variations from one wood to another can be chemometrically analysed using the tools [22].

3. Results and discussion

The PCA result of samples pyrolysed at 500 °C is depicted in Fig. 1. Samples are clearly delineated based on the similarities and dissimilarities of the evolved volatile products. Approximately 80% of the validated variations in all the tested samples are described by 2 PCs. The representation shows an excellent reproducibility of duplicate trials. Hardwoods are largely distinguished from the softwood and the annual plant by PC1 based on the presence of syringyl related components. Although corncob contains small amounts of syringyl related compounds, the quantity of these products such as syringol, 4-allyl syringol and 4-methyl syringol in both beech and albizia was double the amount found in corncob. The position of spruce in PC1 is influenced by high contents of levoglucosan and guaiacyl related volatile components found in the softwood. This is in addition to the absence of syringol related components, which is a characteristic feature of softwoods.

The second PC categorises beech and albizia based on syringyl to guaiacyl ratio. The PC explains about 35% of variations in samples. This ratio is less than 1 in both iroko and corncob but greater than 1 in other hardwoods. The result revealed that iroko is differentiated from other hardwoods because of the presence of resorcinol, p-xylene and 2,6-dimethyl hepta-1,5-diene in high content. The two phenyl bearing compounds are lignin derived phenolic compounds while the 2,6-dimethyl hepta-1,5-diene is thought to be the decomposition product of extractives found only in iroko. Similarly, corncob is differentiated from other samples based on high content of phenol and 4-vinyl phenol. These products are derived from *p*-coumaryl alcohol, a form of lignin moiety largely found in annual plants [21]. It is clear from this result that there exists some dissimilarity in chemical composition of condensable products obtained from fast pyrolysis of different lignocelluloses of even the same class.

3.1. Effect of temperature

The summarised result of samples at different temperatures between 400 and 700 °C is shown in Fig. 2. The categorisation is based on chemical classes of numerous compounds detected. Holocellulose derived volatile products such as acetic acid, non-aromatic aldehydes and ketones are least affected by high temperature. These classes of compounds are readily formed as primary pyrolysis products from biomass. The result shows that their yields seem unabated even at 650–700 °C. This phenomenon could have arisen from the degradation of other heavier products such as anhydrosugar to supplement decomposed fractions of these products. Most abundant compounds in these classes are fragmentation products from pentoses and hexoses. Their formation is therefore ubiquitous so long holocellulosic moieties are present. Also, the thermal liability of pyrans is illustrated in Section 3. While a number of furan related compounds are still detectable at 700 °C, almost all pyran products are hardly found at 650 °C in most samples.

In addition, only 20–40% of initial anhydrosugars found at 400 °C were detectable at 700 °C. The highest residual was found in spruce with no syringyl lignin content. This class of pyrolysis product comprises mostly 1,6-anhydro-β-D-glucopyranose. Their decomposition at high temperature to produce various furans have been noted by previous authors [23]. Guaiacyl and syringyl related volatile products rapidly decayed at high temperature with less than 4% of most fractions detected at 400 °C left at 700 °C in all samples. Instead, the production of benzyl and phenyl related aromatic compound is enhanced.

PCA evaluation of pyrolysis data obtained from different temperature measurements is shown in Fig. 3. This result revealed that pyrolysis at 300 °C and 650–700 °C are least characterised in terms of yield of most volatile products in all samples. There are limited reaction pathways for the formation of volatiles at low temperature. Severe fragmentation of macromolecules occurred at high reaction temperature with possibility of multiple reactions to produce small amount of individual volatile products. Most of these products are non-aromatic aldehydes and ketones. In contrast, the

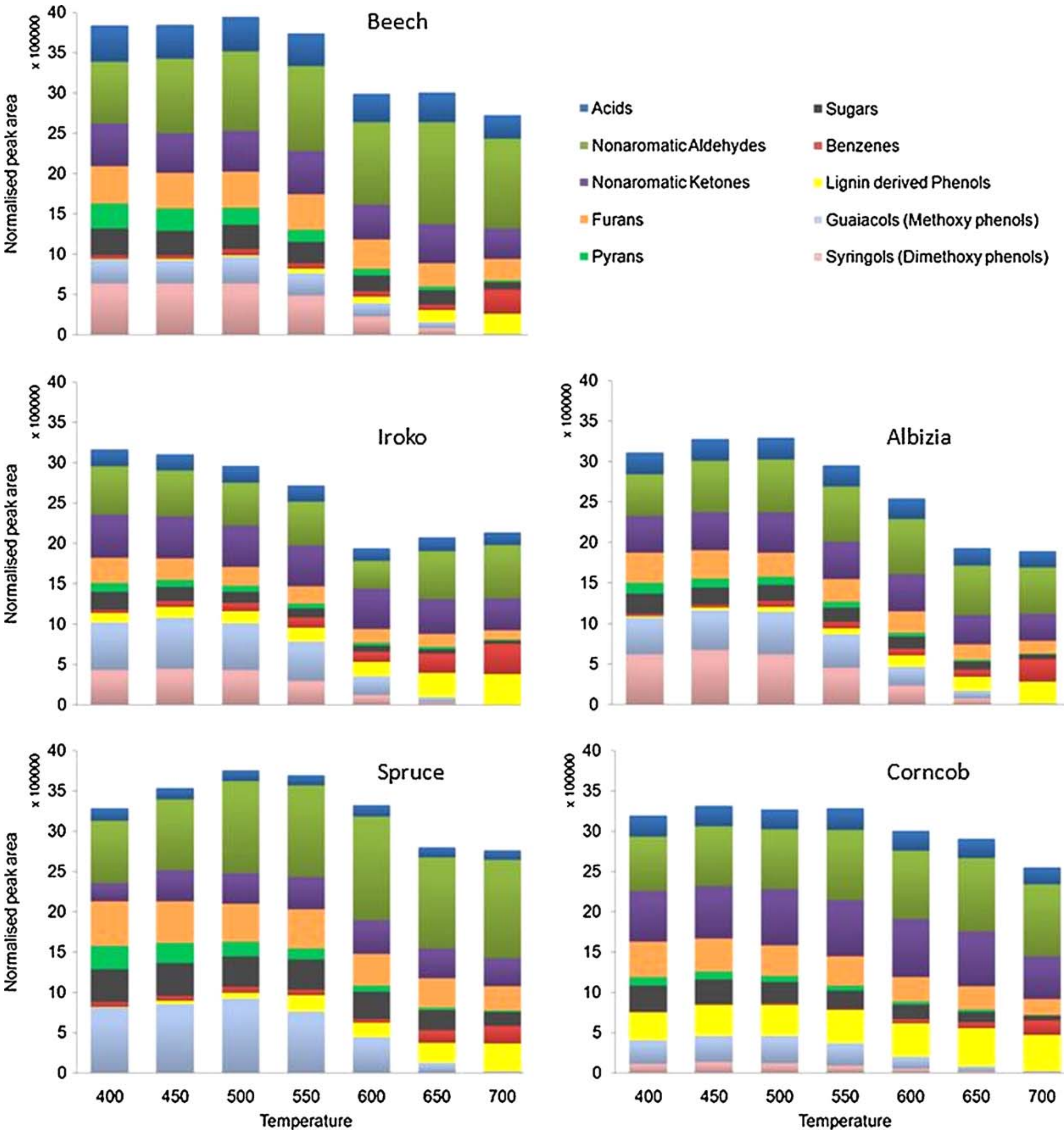

Fig. 2. Volatile products distribution at different temperatures in samples.

temperature range between 400 °C and 500 °C produced the highest concentration of most volatile pyrolysis products.

For clarity, chromatograms of beech for selected temperatures are shown in Fig. 4. Pyrolysis at 300 °C produced the least volatile products due to partial decomposition of the major components. Major chemical changes at low pyrolysis temperature of biomass include partial depolymerisation of polysaccharides and elimination of water from the monosaccharide [24,25]. The limited depolymerisation of macromolecules by bond scission occurs largely within the amorphous hemicellulose and lignin. The overall effect of this partial volatilization is the production of high char content. However, the char content of the residue could not be determined owing to the nature of the pyrolysis unit and sample weight employed.

Still on Fig. 4, peaks of low molecule compounds such as hydroxyl acetaldehyde (**1**) acetic acid (**2**) propanal-2-one and 3-hydroxyl propionaldehyde (**3**) obtained at this temperature are broad and of low mass spectra purity due to overlapping of components. Cellulose, the most abundant component of wood is observed the least decomposed at this temperature. This is evident in the low amount of anhydro-β-D-glucopyranose (**24**) a typical decomposition product from cellulose [25]. However, it could be said that polymeric intermediate products not detectable in GC were formed from glucose at this low temperature. Many peaks were found with obscured identities. However, their MS fragmentation patterns correspond to anhydrosugar. These products are probably oligomeric forms of anhydrosugars. The formation of anhydro-oligosaccharides has been noted to be a major route preceding the formation of smaller products in holocellulose decomposition [26]. These products are formed following depolymerisation reaction. This is possible at low temperature where the degradation of holocellulose occur least by fragmentation reaction.

Apart from decomposition products such as 3-hydroxy-5,6-dihydro-(4H) pyran-4-one (**9**) and dihydro-4-hydroxy-

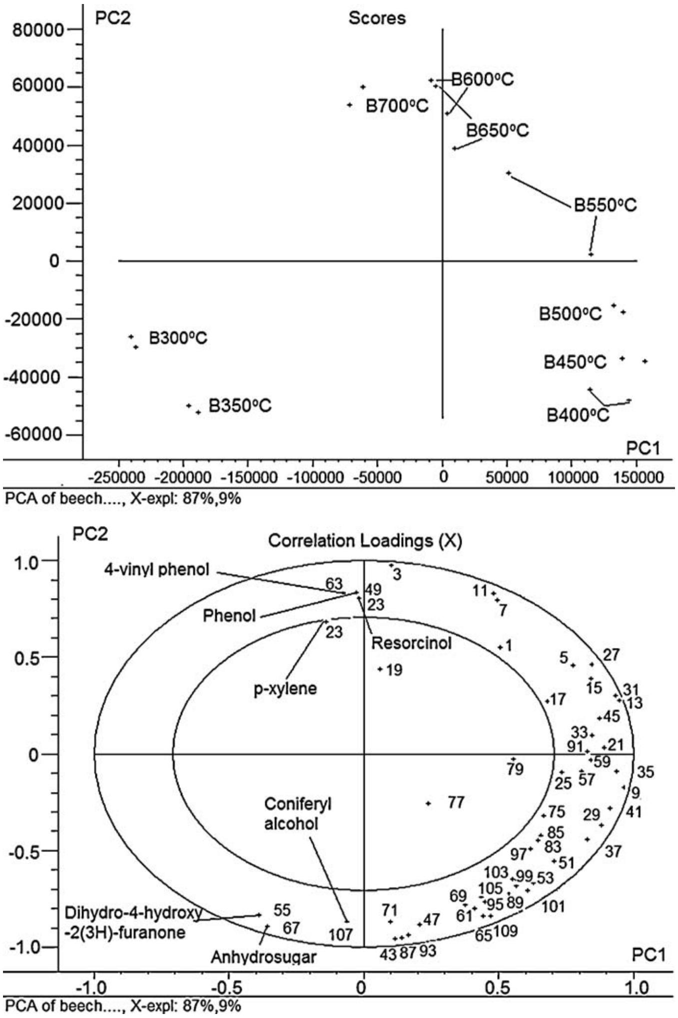

Fig. 3. PCA scores and correlation loadings of Py-GC/MS data from beech pyrolysed at different temperature.

2(3H)-furanone from holocellulose, most prominent peaks (see Figs. 2 and 4) are lignin derived compounds such as 4-vinyl guaiacol (**17**) 4-vinyl syringol (**23**) (trans)-4-(1-propenyl)-syringol (**25**) coniferyl alcohol (**27**) and sinapaldehyde. 4-vinyl phenol is the major lignin related volatile obtained from corncob pyrolysis product. The vinyl related volatiles were probably formed after the decarboxylation of low lignin related species such as sinapic, ferulic and cinnamic acids, covalently associated with the holocellulose. A covalent association between hemicellulose and lignin in biomass has been established by previous authors [27,28]. Sinapyl, coniferyl and p-coumaryl alcohols are main precursors involved in the formation of the lignin monomers. These precursors formed from sinapic, ferulic and cinnamic acids through cinnamate pathway are often found as glucosides in cambial tissue [29]. A further pointer to this assertion is the detection of highest concentration of sinapaldehyde at low pyrolysis temperature. A similar decomposition trend was observed in chromatograms of all samples beside differences occasioned by the dissimilarity in samples' composition.

Products obtained at 350 °C are discriminated from those at 300 °C based on their concentrations. With the exception of anhydro-β-D-glucopyranose, other anhydrosugar such as anhydro-β-D-arabinofuranose, 1,4:3,6-dianhydro-α-D-glucopyranose (**15**) and many unknown anhydrosugars attained maximum concentration at 350 °C, which decreased downward at higher temperature in all samples. The presence of many anhydrosugar and cellobiosan in pyrolysis products has been reported by earlier author [30]. These anhydro-oligosaccharides can decompose through reverse aldolisation and oxidation to form various low molecule products of aldehyde and ketone compounds [13,30].The production of high amount of 1,4:3,6-dianhydro-α-D-glucopyranose at this low temperature could imply that the sugar was formed from the glucose units associated with amorphous hemicellulose structures. Anhydrosugars of hemicelluloses are more easily obtained at lower temperature than anhydro-β-D-glucopyranose from cellulose owing to the high degree of crystalinity and effective hydrogen bonding among cellulose units [20].

On individual volatile products from classes outline in Table 2 and Fig. 2, the amount of non-aromatic aldehyde surged at high pyrolysis temperature of 400 °C, initially owing to the production of hydroxyl acetaldehyde and propanal-2-one. These products are obtained from reducing and non-reducing end of sugar units through reverse aldolisation, another major thermal degradation mechanism of holocellulose [30]. The production of hydroxyl acetaldehyde steadily decayed at elevated temperature. The amount of overall non-aromatic aldehydes appear slightly sustained due to increase in the production of acrolein as the temperature increases. This temperature also favours the production of 3-hydroxy-5,6-dihydro-(4H)-pyran-4-one. Other volatiles that attained their maximum concentration at this temperature include 3,4-dihydro-6-methyl-2H-pyran-2-one, and 5-(hydroxymethyl)dihydro-2(3H)-furanone. These products are often regarded as hemicellulose decomposition markers but a clear demarcation between the decomposition markers for hemicellulose and cellulose is hard to draw owing to the similarity in their pyrolysis products. However volatile compounds such as 5-(hydroxymethyl)dihydro-2(3H)-furanone are produced from hexoses in holocellulose [31]. They could be formed from both hemicellulose and cellulose following keto-enol tautomerism of the sugar which subsequently undergoes condensation and finally cyclization reaction as suggested by previous authors [32]. Furthermore, acetic acid attained its maximum concentration at 400 °C. This acid is obtained from the cleavage of the acetyl group largely found in the glucuronoxylan of hardwood and annual plant [33]. It is however possible to obtain the acid from the oxidation of acetaldehyde or carbonylation of methanol through carbon monoxide, all produced as decomposition products from the pyrolysis of both cellulose and hemicellulose.

The products obtained between 450 °C and 550 °C are relatively similar in all samples apart from minimal concentration changes. With reduction of other anhydrosugars, levoglucosan attained its maximum concentration between 450 °C and 500 °C. Transglycosylation of glucose leading to the formation of levoglucosan as explained by Shafizadeh et al. [34] largely occurred within this temperature range. The formation of the anhydrosugar reduces at higher temperature. Highest amount of levoglucosan is obtained in spruce compared to other biomasses. This observation did not correspond to the difference in their cellulose contents (Table 1). This discrepancy could be explained in the event that mannose, an hexose similar to glucose was also converted to levoglucosan as suggested by Räisänen et al. [35]. However, this argument appears weak considering the conclusions by several authors indicating that the prospect of obtaining levoglucosan from mannose is remote [20,36]. Rather, the monosaccharide yields 1,6 anhydro-β-D-mannopyranose, an anhydrosugar similar to levoglucosan. The difference in both anhydrosugars is the hydroxyl group attached to the carbon next to the anomeric carbon.

Furthermore, galactoglucomannans is the principal hemicellulose in softwood. It comprises of mannose; glucose and galactose in the proportion of 3:1:1 for galactose-rich softwood. For other softwood, the ratio is 4:1:0.1 where the hemicellulose is just known

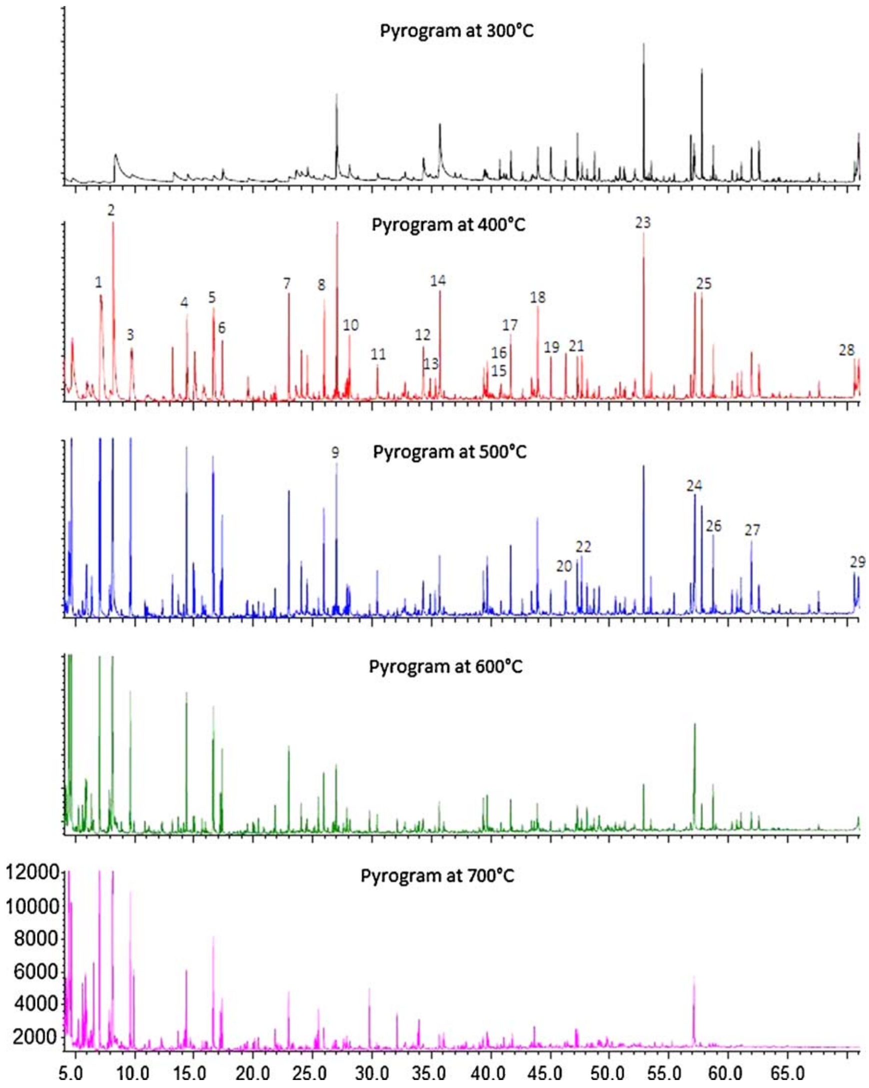

Fig. 4. Beech chromatograms at 300, 400, 500, 600 and 700 °C. List: (**1**) acetaldehyde, hydroxy-; (**2**) acetic acid; (**3**) acetol (hydroxypropanone); (**4**) propionaldehyde, 3-hydroxy; (**5**) oxopropanoic acid methylester; (**6**) furaldehyde, 2-; (**7**) cyclopentene-1-one, 2-hydroxy-2-; (**8**) furanone, 2(5H)-; (**9**) pyran-4-one, 3-hydroxy-5,6-dihydro-(4H)-; (**10**) pyran-2-one, 3,4-dihydro-6-methyl-2H-; (**11**) guaiacol; 12 (S)-(+)-2′,3′-dideoxyribonolactone; (**13**) guaiacol, 4-methyl; (**14**) unknown anhydrosugar; (**15**) dianhydro-mannopyranose, 1,4:3,6-; (**16**) anhydro-β-D-xylofuranose, 1,5-; (**17**) guaiacol, 4-vinyl-; (**18**) Syringol; 19 2(3H)-furanone, dihydro-4-hydroxy-; (**20**) pyran-4-one, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-, (4H)-; (**21**) trans isoeugenol; (**22**) Syringol, 4-methyl; (**23**) syringol, 4-vinyl; (**24**) anhydro-β-D-glucopyranose (levoglucosan); (**25**) syringol, 4-(1-propenyl)-trans; (**26**) syringaldehyde; (**27**) coniferyl alcohol (trans); (**28**) sinapyl alcohol (trans): (**29**) sinapaldehyde (trans).

as glucomannan [29]. As indicated in Table 1, the hemicellulose in spruce contributes substantially high glucose units with low degree of polymerisation (DP) to the total glucose in the biomass compared to hardwood. It can therefore be concluded that the difference in the amount of levoglucosan in the hardwoods and spruce lies in the ease of converting glucose units found in the hemicellulose of spruce to levoglucosan owing to its lower DP compared to cellulose. The high metal content in African biomasses could have played a mitigating role in the formation of this anhydrosugar. This conclusion agrees with the findings of previous authors [17,21].

At the temperature of 650–700 °C, non-aromatic aldehydes and ketones and furans dominate the chromatograms in all samples where pyrans are produced less. Holocellulose appears to have been converted to low molecular products and gases such as CO_2 and CO through severe fragmentation mechanisms. Both guaiacols and syringols were least visible in chromatograms (Fig. 4). Instead, numerous benzyl and phenyl based products were formed. These products were probably formed from the combination of methyl and hydroxyl radicals (produced from severe homolytic degradation) with the aromatic ring from demethoxylated lignin (after the cleavage of α and β-aryl-alkyl-ether linkages). The occurrence of cyclization and other rearrangement reactions could have led to the production of closed ring products such as naphthalene.

Interestingly, both 6-hydroxy-7-methoxy-1H-indene and 6-hydroxy-7-methoxy-2H-indene were found in all samples while only samples with syringyl units contained 6-hydroxy-5,7-dimethoxy-1H-indene. These products are also detected at 300 °C, maintaining their maximum concentration between 450 °C and 550 and sparingly formed at 650–700 °C. It is established from these observations that indene related compounds are products related to biomass lignin components.

3.2. *Effect of sample pre-treatment*

To investigate the influence of the alkali and earth metals contents on the nature of volatile products, all samples were washed with dilute acid or water. Alkali and alkaline earth metals are exchangeable ions bounded to biomasses and can easily be removed by treatment with water or diluted acid [19]. Treated samples were pyrolysed at 500 °C and results obtained for hardwoods

Table 2
Normalised peak area of beech wood volatile products at different temperatures Beech.

Compound	Temperature (°C)						
	400	450	500	550	600	650	700
(i) Beech							
Acids							
Acetic acid	45.9	42.4	43.3	41.0	36.5	36.2	28.8
Nonaromatic aldehydes							
Propenal, 2-(acrolein)	–	–	11.6	19.3	25.5	32.5	31.7
Acetaldehyde, hydroxy-	42.2	48.0	39.7	37.4	13.9	25.6	13.6
Methylglyoxal (Propanal-2-one)	23.5	20.8	21.9	22.0	20.1	17.0	11.0
Propionaldehyde, 3-hydroxy-	10.5	11.2	11.6	11.5	9.6	8.4	5.3
Nonaromatic ketones							
Acetol (hydroxypropanone)	18.2	16.8	16.5	16.2	10.3	14.1	10.5
Butandione, 2,3-; (diacetyl)	6.4	7.0	7.7	9.0	5.9	5.8	4.5
Butenal-2-one, 3-	9.7	5.1	3.1	1.9	1.3	0.7	0.5
3-Pentanone	4.9	3.8	4.4	4.2	3.5	2.6	1.4
Cyclopenten-1-one, 2-	–	1.8	2.4	2.8	2.8	2.9	2.9
Cyclopenten-1-one, 2-hydroxy-2-	10.5	9.4	9.9	10.3	6.8	7.4	4.4
Furans							
Furanone, 2(5H)-	9.3	8.4	8.5	6.9	5.1	3.4	1.9
Furaldehyde, 2-	7.0	6.3	6.7	6.5	6.1	4.7	3.7
Furaldehyde, 5-(hydroxymethyl)-, 2-	2.7	2.5	2.5	2.2	1.2	1.4	1.0
2(3H)-Furanone, dihydro-4-hydroxy-	4.0	2.9	2.2	1.7	1.2	0.9	0.5
5-(Hydroxymethyl)dihydro-2(3H)-furanone	6.9	5.2	4.6	3.9	2.2	2.2	0.9
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	17.5	15.3	12.6	9.6	5.2	3.0	0.8
Sugars							
Anhydro-β-D-arabinofuranose, 1,5-	0.8	0.7	0.6	0.5	0.3	0.5	–
Anhydro-β-D-glucopyranose, 1,6-; (levoglucosan)	15.1	15.6	18.2	17.7	15.3	14.2	9.3
Dianhydro-α-D-glucopyranose, 1,4:3,6-	1.6	1.3	1.2	1.0	0.8	0.6	0.4
Benzenes							
Indene, 6-hydroxy-7-methoxy-, 1H-	0.9	–	2.0	1.9	1.2	–	–
Indene, 6-hydroxy-7-methoxy-, 2H-	1.6	2.0	2.8	2.8	1.9	0.8	–
Indene, 6-hydroxy-5,7-dimethoxy-, 1H-	2.0	2.2	2.5	1.7	0.7	–	–
Lignin derived phenols							
Cresol, o-	–	0.6	0.8	1.1	1.3	2.0	2.8
Cresol, m-	–	–	–	0.6	0.8	0.8	2.2
Guaiacols (methoxy phenols)							
Guaiacol	4.3	3.7	3.5	2.9	1.6	0.9	0.6
Guaiacol, 4-vinyl-	4.9	4.6	5.0	4.4	2.6	1.2	–
Guaiacol, 4-propenyl-(trans); (isoeugenol)	4.9	3.3	4.0	3.3	2.1	1.1	–
Coniferyl alcohol (trans)	4.6	6.3	6.9	5.3	1.9	–	–
Syringols (dimethoxy phenols)							
Syringol	7.1	6.7	6.8	5.0	2.2	0.8	–
Syringol, 4-vinyl-	12.4	11.1	10.5	7.8	3.7	1.4	–
Syringol, 4-(1-propenyl)-, trans	8.2	7.8	8.1	5.3	2.1	0.6	–
Sinapaldehyde (trans)	8.0	7.4	7.1	5.5	2.7	0.7	–
Spruce							
Acids							
Acetic acid	16.0	14.4	13.9	13.4	13.3	11.9	11.4
Nonaromatic aldehydes							
Propenal, 2-(acrolein)	–	–	12.7	20.5	28.4	30.5	34.0
Acetaldehyde, hydroxy-	48.6	51.8	47.0	42.6	29.5	17.6	18.6
Propanal-2-on (Methylglyoxal)	22.2	23.5	22.3	22.5	21.3	17.5	11.6
Propionaldehyde, 3-hydroxy-	6.5	7.2	7.2	7.1	6.3	5.0	3.7
Nonaromatic ketones							
Hydroxypropanone (acetol)	15.0	14.8	13.4	13.0	12.3	10.6	11.3
Butandione, 2,3-; (diacetyl)	–	7.3	7.3	8.4	6.0	5.3	4.8
Butenal-2-one, 3-	–	2.5	2.9	2.1	1.1	0.5	0.4
3-Pentanone	–	–	–	–	–	–	–
Cyclopenten-1-one, 2-	–	1.6	2.0	2.4	2.7	2.8	0.9
Cyclopenten-1-one, 2-hydroxy-2-	8.0	8.2	8.5	8.6	8.1	6.3	4.9
Furans							
Furanone, 2(5H)-	7.2	6.8	6.9	5.7	4.3	2.9	1.9
Furaldehyde, 2-	4.6	4.7	5.0	5.2	4.8	4.1	3.4
Furaldehyde, 5-(hydroxymethyl)-, 2-	6.5	6.6	6.0	5.8	4.3	3.0	2.2
2(3H)-Furanone, dihydro-4-hydroxy-	6.2	4.6	2.8	1.8	0.4	1.2	0.8
5-(Hydroxymethyl)dihydro-2(3H)-furanone	5.9	4.6	3.6	3.1	2.2	1.3	0.8
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	9.1	8.4	7.0	5.4	3.5	1.2	0.5
Sugars							
Anhydro-β-D-arabinofuranose, 1,5-	2.0	1.8	1.5	1.3	0.9	0.8	–
Anhydro-β-D-glucopyranose, 1,6-; (levoglucosan)	26.0	29.8	29.8	29.1	28.1	23.4	16.5
Dianhydro-α-D-glucopyranose, 1,4:3,6-	1.0	0.9	0.8	0.8	0.6	0.5	0.3
Benzenes							
Indene, 6-hydroxy-7-methoxy-, 1H-	2.3	2.5	3.2	2.8	1.5	0.5	–
Indene, 6-hydroxy-7-methoxy-, 2H-	3.0	3.2	3.8	3.4	1.9	–	–
Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	–	–	–	–	–	–	–

Table 2 (*Continued*)

Compound	Temperature (°C)						
	400	450	500	550	600	650	700
Lignin derived phenols							
Cresol, o-	–	0.9	1.1	1.4	1.9	2.5	3.6
Cresol, m-	–	0.5	0.6	0.8	1.1	1.7	2.6
Guaiacols (methoxy phenols)							
Guaiacol	8.6	8.8	8.1	6.0	3.2	1.2	0.3
Guaiacol, 4-vinyl-	10.7	11.6	11.6	10.2	5.7	2.1	–
Guaiacol, 4-propenyl-(trans); (isoeugenol)	9.5	10.3	10.4	8.3	5.2	1.8	–
Coniferyl alcohol (trans)	12.1	11.5	16.4	12.0	5.1	–	–
Syringols (dimethoxy phenols)							
Syringol	–	–	–	–	–	–	–
Syringol, 4-vinyl-	–	–	–	–	–	–	–
Syringol, 4-(1-propenyl)-, trans	–	–	–	–	–	–	–
Sinapaldehyde (trans)	–	–	–	–	–	–	–
(iii) Iroko							
Acids							
Acetic acid	21.4	20.5	20.0	19.3	19.8	16.1	14.9
Nonaromatic aldehydes							
Propenal, 2-(acrolein)	–	–	–	8.4	13.6	15.1	18.5
Acetaldehyde, hydroxy-	32.0	29.3	24.6	19.1	14.8	9.3	9.5
Propanal-2-on (methylglyoxal)	15.3	13.1	13.4	13.3	13.6	9.9	6.0
Propionaldehyde, 3-hydroxy-	4.7	4.9	4.9	4.7	4.6	3.2	2.5
Nonaromatic ketones							
Hydroxypropanone (acetol)	19.9	19.3	17.3	15.3	14.2	10.6	10.0
Butandione, 2,3-; (diacetyl)	4.5	4.7	5.6	4.9	5.2	4.3	3.3
Butenal-2-one, 3-	1.8	2.0	1.7	1.4	0.8	0.3	–
3-Pentanone	6.9	6.1	5.7	4.9	4.4	2.7	1.5
Cyclopenten-1-one, 2-	1.2	1.7	2.2	2.6	2.9	2.6	2.6
Cyclopenten-1-one, 2-hydroxy-2-	13.2	11.6	9.8	8.3	7.5	5.1	3.9
Furans							
Furanone, 2(5H)-	7.5	6.7	5.6	4.6	3.7	2.2	1.3
Furaldehyde, 2-	3.6	3.9	4.0	4.1	4.1	3.1	2.4
Furaldehyde, 5-(hydroxymethyl)-, 2-	0.8	0.8	0.8	0.6	0.5	0.5	0.5
2(3H)-Furanone, dihydro-4-hydroxy-	1.9	1.7	1.8	1.6	1.2	–	–
5-(Hydroxymethyl)dihydro-2(3H)-furanone	4.0	2.9	2.0	1.4	1.2	0.6	–
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	4.3	3.7	2.7	2.0	1.4	0.6	0.2
Sugars							
Anhydro-β-D-arabinofuranose, 1,5-	0.5	0.4	0.4	0.3	0.4	–	–
Anhydro-β-D-glucopyranose, 1,6-; (levoglucosan)	3.2	3.7	4.2	4.3	3.5	4.0	2.9
Dianhydro-α-D-glucopyranose, 1,4:3,6-	0.9	0.8	0.8	0.7	0.7	0.6	0.4
Benzenes							
Indene, 6-hydroxy-7-methoxy-, 1H-	0.8	1.2	2.3	2.2	1.5	–	–
Indene, 6-hydroxy-7-methoxy-, 2H-	1.0	1.5	2.6	2.7	2.1	–	–
Indene, 6-hydroxy-5,7-dimethoxy-, 1H-	0.7	1.1	1.4	1.0	0.6	–	–
Lignin derived phenols							
Cresol, o-	0.9	1.2	1.4	1.7	2.3	2.5	3.3
Cresol, m-	0.6	0.7	0.8	0.9	1.5	1.8	2.6
Guaiacols (methoxy phenols)							
Guaiacol	8.9	9.4	8.8	7.0	4.0	1.4	–
Guaiacol, 4-vinyl-	15.0	15.5	14.6	11.4	6.7	2.1	0.4
Guaiacol, 4-propenyl-(trans); (isoeugenol)	6.6	7.7	7.7	6.2	4.1	–	–
Coniferyl alcohol (trans)	12.3	13.6	10.8	8.0	3.1	–	–
Syringols (dimethoxy phenols)							
Syringol	6.6	6.7	6.2	4.3	2.1	0.5	–
Syringol, 4-vinyl-	13.8	13.4	11.8	8.2	3.9	0.9	–
Syringol, 4-(1-propenyl)-, trans	5.9	6.2	5.6	3.8	1.7	0.4	–
Sinapaldehyde (trans)	2.5	2.4	2.7	2.0	0.8	–	–
(iv) Albizia							
Acids							
Acetic acid	27.4	27.2	27.2	26.9	25.4	21.7	20.6
Nonaromatic aldehydes							
Propenal, 2-(acrolein)	–	5.3	9.4	14.0	18.7	21.7	24.0
Acetaldehyde, hydroxy-	22.3	25.5	18.8	17.0	14.5	9.1	8.3
Propanal-2-on (Methylglyoxal)	15.2	13.2	15.6	16.1	15.9	14.3	10.5
Propionaldehyde, 3-hydroxy-	4.7	5.2	5.8	5.7	5.0	4.2	3.4
Nonaromatic ketones							
Hydroxypropanone (acetol)	12.8	13.4	13.4	12.5	11.7	8.8	9.3
Butandione, 2,3-; (diacetyl)	4.7	4.9	6.6	5.4	5.2	4.6	4.1
Butenal-2-one, 3-	1.7	2.3	2.8	2.1	1.0	0.6	0.4
3-Pentanone	8.0	7.5	6.7	6.1	4.9	3.2	2.0
Cyclopenten-1-one, 2-	1.2	1.6	2.2	2.4	2.5	2.4	2.5
Cyclopenten-1-one, 2-hydroxy-2-	10.9	10.3	9.3	8.3	7.1	4.9	4.0
Furans							
Furanone, 2(5H)-	7.3	6.5	7.0	5.8	4.4	3.1	1.7
Furaldehyde, 2-	4.7	4.3	4.8	4.7	4.1	3.4	2.6

Table 2 (*Continued*)

Compound	Temperature (°C)						
	400	450	500	550	600	650	700
Furaldehyde, 5-(hydroxymethyl)-, 2-	1.1	1.2	1.0	0.8	0.6	0.4	0.5
2(3H)-Furanone, dihydro-4-hydroxy-	2.5	2.2	–	–	–	0.9	0.6
5-(Hydroxymethyl)dihydro-2(3H)-furanone	–	–	–	–	–	–	–
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	9.5	8.4	7.2	5.6	3.7	1.8	0.6
Sugars							
Anhydro-β-D-arabinofuranose, 1,5-	0.7	0.7	0.7	0.7	0.7	–	–
Anhydro-β-D-glucopyranose, 1,6-; (levoglucosan)	7.0	8.0	9.4	9.3	8.6	6.3	5.8
Dianhydro-α-D-glucopyranose, 1,4:3,6-	0.8	0.8	0.8	0.7	0.7	0.5	0.4
Benzenes							
Indene, 6-hydroxy-7-methoxy-, 1H-	0.8	0.9	2.3	2.7	1.5	0.5	–
Indene, 6-hydroxy-7-methoxy-, 2H-	0.9	1.2	2.6	3.4	2.2	1.1	0.8
Indene, 6-hydroxy-5,7-dimethoxy-, 1H-	1.3	1.5	2.4	1.8	0.7	–	–
Lignin derived phenols							
Cresol, o-	0.5	0.7	1.0	1.1	1.6	1.9	2.9
Cresol, m-	–	0.5	0.6	0.7	1.2	1.7	2.5
Guaiacols (methoxy phenols)							
Guaiacol	6.9	7.4	7.5	5.4	3.0	1.4	–
Guaiacol, 4-vinyl-	8.3	8.8	8.6	7.2	4.2	1.9	0.5
Guaiacol, 4-propenyl-(trans); (Isoeugenol)	6.8	7.5	8.1	6.6	4.1	2.5	–
Coniferyl alcohol (trans)	11.6	11.4	11.3	7.1	3.1	–	–
Syringols (dimethoxy phenols)							
Syringol	9.6	10.5	9.8	7.1	3.1	1.0	–
Syringol, 4-vinyl-	15.3	15.1	13.4	9.4	4.4	1.6	–
Syringol, 4-(1-propenyl)-, trans	10.2	10.8	9.8	6.1	2.6	0.7	–
Sinapaldehyde (trans)	4.7	4.6	4.7	3.3	1.6	–	–
(v) Corncob							
Acids							
Acetic acid	26.8	25.5	25.6	26.1	24.2	23.2	19.4
Nonaromatic aldehydes							
Propenal, 2-(acrolein)	–	–	–	13.0	19.3	26.0	26.3
Acetaldehyde, hydroxy-	31.8	32.4	28.1	25.2	19.8	20.8	9.9
Propanal-2-on (methylglyoxal)	20.8	23.7	24.4	26.3	24.4	20.8	13.1
Propionaldehyde, 3-hydroxy-	4.9	5.5	5.8	5.9	5.4	4.9	3.2
Nonaromatic ketones							
Hydroxypropanone (acetol)	21.7	22.3	21.3	20.3	18.3	18.6	13.0
Butandione, 2,3-; (diacetyl)	4.9	6.4	8.2	7.6	8.0	7.6	5.8
Butenal-2-one, 3-	1.9	2.5	2.6	2.4	1.2	0.5	0.3
3-Pentanone	9.2	8.8	8.1	7.2	6.0	4.1	2.3
Cyclopenten-1-one, 2-	1.5	2.2	2.7	3.2	3.4	3.4	3.2
Cyclopenten-1-one, 2-hydroxy-2-	13.9	12.9	12.1	11.7	10.2	8.9	5.2
Furans							
Furanone, 2(5H)-	7.3	7.1	6.9	6.5	4.5	3.0	1.7
Furaldehyde, 2-	6.1	6.0	6.3	6.6	5.9	5.0	3.7
Furaldehyde, 5-(hydroxymethyl)-, 2-	1.1	1.2	1.0	0.9	0.7	0.7	0.5
2(3H)-Furanone, dihydro-4-hydroxy-	1.4	1.2	0.9	0.9	0.7	0.5	–
5-(Hydroxymethyl)dihydro-2(3H)-furanone	–	–	–	–	–	–	–
Pyrans							
Pyran-4-one, 3-hydroxy-5,6-dihydro-, (4H)-	8.0	7.4	5.7	4.7	2.9	1.6	0.2
Sugars							
Anhydro-β-D-arabinofuranose, 1,5-	3.6	3.3	3.2	2.6	1.7	1.2	0.8
Anhydro-β-D-glucopyranose, 1,6-; (levoglucosan)	4.4	6.1	5.9	5.9	5.5	4.7	2.6
Dianhydro-α-D-glucopyranose, 1,4:3,6-	1.3	1.2	1.3	1.2	1.0	0.8	0.6
Benzenes							
Indene, 6-hydroxy-7-methoxy-, 1H-	0.3	0.5	0.7	1.0	0.5	–	–
Indene, 6-hydroxy-7-methoxy-, 2H-	0.3	0.6	0.8	–	0.7	–	–
Indene, 6-Hydroxy-5,7-dimethoxy-, 1H-	–	0.5	0.6	0.5	0.2	–	–
Lignin derived phenols							
Cresol, o-	0.5	1.2	0.8	1.0	1.8	2.2	2.4
Cresol, m-	0.6	0.7	0.7	0.9	1.0	1.5	1.6
Guaiacols (methoxy phenols)							
Guaiacol	5.1	5.6	5.6	4.5	2.5	1.1	0.6
Guaiacol, 4-vinyl-	17.8	19.3	19.4	16.1	8.9	3.5	–
Guaiacol, 4-propenyl-(trans); (isoeugenol)	–	–	–	–	–	–	–
Coniferyl alcohol (trans)	1.5	1.6	1.8	–	–	–	–
Syringols (dimethoxy phenols)							
Syringol	3.4	3.7	3.5	2.5	1.1	0.4	0.7
Syringol, 4-vinyl-	2.9	3.1	2.9	2.2	1.0	0.3	–
Syringol, 4-(1-propenyl)-, trans	2.2	2.4	2.2	1.5	0.7	0.2	–
Sinapaldehyde (trans)	0.6	0.5	0.4	–	–	–	–

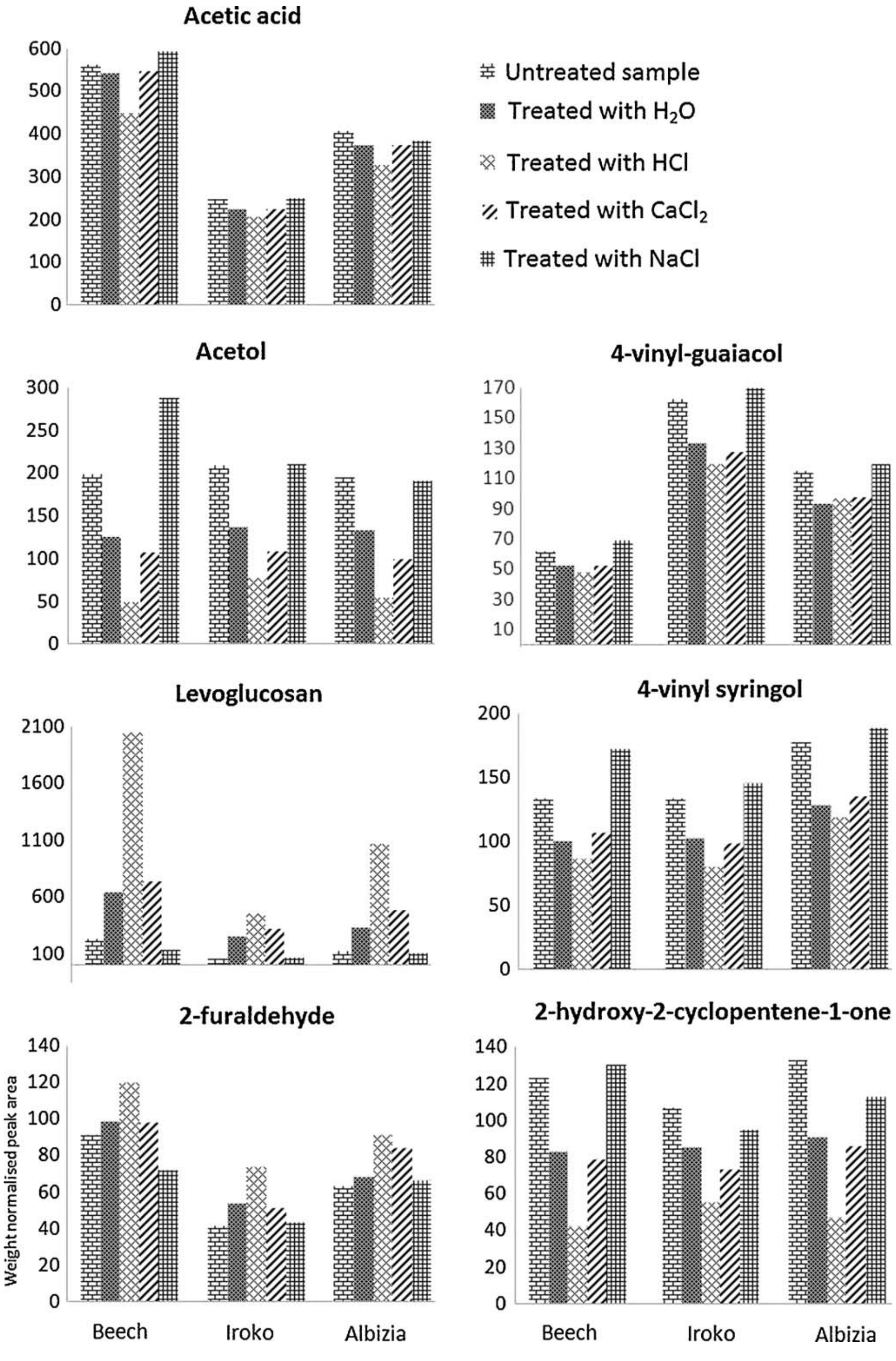

Fig. 5. Effects of pre-treatments on some volatile products.

are shown in Fig. 5. The removal resulted in the reduction of most holocellulose-derived low molecular products but with only slight effect on the yield of acetic acid. The effect is severer in samples treated with acid due to more effective removal of the indigenous metal with dilute acid. In both cases, it is observed that the decomposition reactions occurred predominantly via depolymerisation and dehydration processes. This remark is buttressed by the increase in yields of anhydrosugars and high molecular furan and pyran products.

Product such as 1-hydroxy-2-butanone, largely found in African biomasses, was probably formed in the pyrolysate due to metal contents in the biomasses. This assertion is confirmed by the reduction in the product's yield by 37–50% and 71–89% in water and acid washed samples respectively. Similar phenomenon was observed in 2-hydroxy-2-cyclopentene-1-one, acetol and other related products. To determine the metal ion responsible, samples were impregnated with 0.1 M NaCl and $CaCl_2$ as previously described and pyrolysed. The result obtained (as shown in Fig. 5

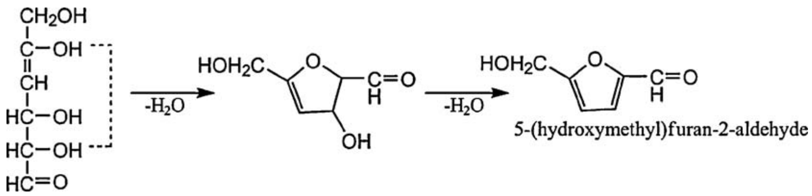

Fig. 6. Suggested pathway for the formation of 5-(hydroxymethyl) furan-2-aldehyde from hexose sugar.

indicates that the monovalent metals (especially potassium)) with high concentration in the African biomasses largely induced the formation of these low molecular products. The removal of the metals resulted in slight reduction in the yield of lignin derived products such as vinyls of guaicol and syringol. These products are often most abundant lignin derived fractions from lignocellulose pyrolysis. However, concentrations of some other lignin products such as 4-methyls of guaiacol and syringol slightly improved upon the removal of metals with diluted acids.

The most significant effect of washing all the samples is the remarkable increase in the amount of volatile products such as furan-2-aldehyde, 5-(hydroxymethyl) furan-2-aldehyde, levoglucosan and other anhydrosugars. This is considerably high in anhydrosugars especially levoglucosan up to 9 times increase in samples washed with dilute acid. Fahmi et al. [18] had previously noted that the removal of metals from biomass sample correlates with increase in the average molecular weight (M_w) of the liquid product. This observation is due to increase in the formation of heavy molecular anhydrosugars and pyrans. Alkaline earth metal (such as Ca^+) seemed to have played positive roles in decomposition processes through which these products are favourably formed.

However, the removal of native metal ions did not result in any preferential enhancement in the yield of related products in African biomasses compared to the European hardwood. This is probably due to the presence of other metals that cannot be removed by these pretreatment methods such as aluminium found in large concentration in the African biomass [21]. It can therefore be concluded that the pre treatment would not cause African biomasses to have equivalent volatile products yield compared with European, although they all have similar holocellulose contents.

Furthermore, the relative amount of both [21] 5-(hydroxymethyl) furan-2-aldehyde and 1,6-β-D-anhydroglucopyranose largely correspond among all sample and both showed similar response in all treated samples leading to the conclusion that both were probably formed through parallel pathways from hexose sugars. In the previous work of Shafizadeh [37], it was observed that levoglucosenone yielded 5-(hydroxymethyl) furan-2-aldehyde on reaction with heated aqueous mineral acid. However, a positive correlation (0.7–0.9) between both established in all samples could be suggestive that they were probably formed concurrently. Based on the template of Richards and Shafizadeh [32], a suggestive pathway for the formation of the former is depicted in Fig. 6.

4. Conclusions

The severity of the homolytic and heterolytic fragmentation occasioned by pyrolysis temperature and the chemical composition of biomass determine various decomposition products formed during fast pyrolysis. The presence of aromatic related structures even at low temperature is suggestive of the thermal lability of α-O and β-O bonds within the lignin structure of biomass. Depolymerisation of sugar cellulose effectively occurred within temperature range of 450–550 °C which yielded largest amount of levoglucosan and other low molecule volatiles in all samples. Fast pyrolysis of biomass at temperatures above 600 °C showed increased tendency in the formation of low molecular products of non-aromatic aldehydes and ketones. It also favours the formation of aromatic products which are closely related to lignin units in the biomasses. They are most probably formed from reaction between the demethoxylated phenyl species and alkyl radicals followed by rearrangement reactions. A clear pointer to this assertion is the formation of indene based products whose dimethoxy product was only found in biomass with corresponding syringyl unit. The removal of alkali and earth metals from biomasses showed increase in anhydrosugars, high molecular furan and pyran products but reduction in the low molecular products from holocellulose. The selective effect of these metals in influencing certain volatile products is a tool that can be used to optimise production of desired products for green chemical application in industries.

Acknowledgments

The authors appreciate the financial assistance rendered by Deutscher Akademischer Austauschdienst (DAAD), Germany for awarding PhD scholarship to Mr. Azeez. We equally thank the workers in the wood chemistry technology unit of the Johann Heinrich von Thünen-Institut (vTi), Hamburg for their assistance in the course of the research.

References

[1] A.V. Bridgwater, Catalysis Today 29 (1996) 285–295.
[2] F. Cherubini, G. Jungmeier, M. Wellisch, T. Willke, I. Skiadas, R.V. Ree, E.d. Jong, Biofuels Bioproducts and Biorefining 3 (2009) 534–546.
[3] S.P. Zhang, Y.J. Yan, J.W. Ren, T.C. Li, Energy Sources 25 (2003) 57–65.
[4] A.V. Bridgwater, Journal of Analytical and Applied Pyrolysis 51 (1999) 3–22.
[5] A. Oasmaa, Y. Solantausta, V. Arpiainen, E. Kuoppala, K. Sipilä, Energy & Fuels (2009).
[6] L.K. Mok, R.G. Graham, B.A. Freel, M.A. Bergougnou, R.P. Overend, Journal of Analytical and Applied Pyrolysis 8 (1985) 391–400.
[7] T.P. Vispute, G.W. Huber, International Sugar Journal 110 (2008) 138–149.
[8] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Journal of Analytical and Applied Pyrolysis 86 (2009) 323–330.
[9] R.J.M. Westerhof, D.W.F. Brilman, W.P.M. van Swaaij, S.R.A. Kersten, Industrial & Engineering Chemistry Research 49 (2009) 1160–1168.
[10] S.H. Jung, B.S. Kang, J.S. Kim, Journal of Analytical and Applied Pyrolysis 82 (2008) 240–247.
[11] M. Garcia-Perez, X.S. Wang, J. Shen, M.J. Rhodes, F.J. Tian, W.J. Lee, H.W. Wu, C.Z. Li, Industrial & Engineering Chemistry Research 47 (2008) 1846–1854.
[12] M. Balat, Energy Sources Part a –– Recovery Utilization and Environmental Effects 30 (2008) 620–635.
[13] F. Shafizadeh, Y.L. Fu, Carbohydrate Research 29 (1973) 113–122.
[14] H.P. Yang, R. Yan, H.P. Chen, D.H. Lee, C.G. Zheng, Fuel 86 (2007) 1781–1788.
[15] C. Fushimi, S. Katayama, K. Tasaka, M. Suzuki, A. Tsutsumi, AIChE Journal 55 (2009) 529–537.
[16] T. Hosoya, H. Kawamoto, S. Saka, Journal of Wood Science 53 (2007) 351–357.
[17] G.N. Richards, G.C. Zheng, Journal of Analytical and Applied Pyrolysis 21 (1991) 133–146.
[18] R. Fahmi, A. Bridgwater, I. Donnison, N. Yates, J.M. Jones, Fuel 87 (2008) 1230–1240.
[19] M. Kleen, G. Gellerstedt, Journal of Analytical and Applied Pyrolysis 35 (1995) 15–41.
[20] J. Kelly, M. Mackey, R.J. Helleur, Journal of Analytical and Applied Pyrolysis 19 (1991) 105–117.
[21] A.M. Azeez, D. Meier, J.r. Odermatt, T. Willner, Energy & Fuels 24 (2010) 2078–2085.
[22] A. Alves, N. Gierlinger, M. Schwanninger, J. Rodrigues, Journal of Analytical and Applied Pyrolysis 85 (2009) 30–37.
[23] T.R. Carlson, J. Jae, Y.-C. Lin, G.A. Tompsett, G.W. Huber, Journal of Catalysis 270 (2010) 110–124.

[24] A.D. Pouwels, J.J. Boon, Journal of Analytical and Applied Pyrolysis 17 (1990) 97–126.
[25] F. Shafizadeh, Journal of Analytical and Applied Pyrolysis 3 (1982) 283–305.
[26] A.D. Pouwels, G.B. Eijkel, P.W. Arisz, J.J. Boon, Journal of Analytical and Applied Pyrolysis 15 (1989) 71–84.
[27] C. Lapierre, B. Pollet, M.-C. Ralet, L. Saulnier, Phytochemistry 57 (2001) 765–772.
[28] L. Saulnier, M.-J. Crépeau, M. Lahaye, J.-F. Thibault, M.T. Garcia-Conesa, P.A. Kroon, G. Williamson, Carbohydrate Research 320 (1999) 82–92.
[29] E. Sjöström, Wood Chemistry: Fundamentals and Applications, Academic Press Ltd., London, 1993.
[30] J.A. Lomax, J.M. Commandeur, P.W. Arisz, J.J. Boon, Journal of Analytical and Applied Pyrolysis 19 (1991) 65–79.
[31] D.R. Budgell, E.R. Hayes, R.J. Helleur, Analytica Chimica Acta 192 (1987) 243–253.
[32] G.N. Richards, F. Shafizadeh, Carbohydrate Research 106 (1982) 83–91.
[33] A. Aho, N. Kumar, K. Eranen, B. Holmbom, M. Hupa, T. Salmi, D.Y. Murzin, International Journal of Molecular Sciences 9 (2008) 1665–1675.
[34] F. Shafizadeh, R.H. Furneaux, T.G. Cochran, J.P. Scholl, Y. Sakai, Journal of Applied Polymer Science 23 (1979) 3525–3539.
[35] U. Räisänen, I. Pitkänen, H. Halttunen, M. Hurtta, Journal of Thermal Analysis and Calorimetry 72 (2003) 481–488.
[36] R.H. Furneaux, F. Shafizadeh, Carbohydrate Research 74 (1979) 354–360.
[37] F. Shafizadeh, R.H. Furneaux, T.T. Stevenson, Carbohydrate Research 71 (1979) 169–191.

Journal of Analytical and Applied Pyrolysis 91 (2011) 296–302

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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Effects of zeolites on volatile products of beech wood using analytical pyrolysis

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ARTICLE INFO

Article history:
Received 16 December 2010
Accepted 10 March 2011
Available online 21 March 2011

Keywords:
Zeolite
Levoglucosan
Furfural
Holocellulose
Py-GC/MS
Volatile Product
Acid
Selectivity
Lignin
Wood

ABSTRACT

Five unmodified basic and acidic zeolites have been tested in the thermo-chemical conversion of beech (*Fagus sylvatica* L.) using an on-line pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) system to study their effects on lignocellulose thermal degradation products. The catalysts employed were SN-27, MSN-15, MSM-15, H-ZSM-5-28 and H-ZSM-5-80 with varying Si/Al ratio between 11 and 80. Thoroughly mixed samples of the biomass with different catalysts loading were pyrolysed at 500 °C. The catalyst exhibited varying degree of selectivity on individual volatile products. The selectivity was largely controlled by the nature of zeolites' active sites and alumina contents. The acidic catalysts mostly influenced the condensable organic products; induced high yields of furfural and levoglucosan. Their yields increased up to five and nine times respectively in samples spiked with 40% MSM-15 and H-ZMS-5 on the basis of feedstock weight. H-ZSM-5 with lower alumina content proved most effective in enhancing high yield of furfural due to better diffusion of molecules through the pores. A slight reduction in polysaccharide derived low molecular volatiles such as hydroxyacetaldehyde, acetic acid, hydroxypropanone was observed in all catalysts. The overall result indicated that the acidic catalysts largely induced cleavage of glycosidic bonds through protonation predominantly on zeolites' surface area. This was followed by the modification of free hydroxyl groups through dehydration process. All zeolites revealed no significant effect on most lignin derived products except indenes.

1. Introduction

The role of biomass in generating fuel as well as potential raw materials for producing chemicals with low sulphur base content has continued to generate interest in the search for alternative renewable energy source since the last two decades. Fast pyrolysis is one of the well established means of converting various forms of biomasses to obtain organic liquid called bio oil, which is a combination of numerous chemical products obtained from thermal degradation process. Some of these chemicals are important and valuable products in chemical industries [1]. The production of oxygenated chemical species such as glyoxal, hydroxyacetaldehyde, sugars phenols and different aromatics from biomasses possesses great economic potential and wide industrial applications if these products yield and purity from biomasses can be enhanced [2,3]. This view coincides with the current thought on the development of bio-refinery to fully harness the potential of converting biomass feedstocks to fuels and chemicals [4]. The integration of fast pyrolysis process into the biorefinery concept can enhance total utilisation of lignocellulosic feedstocks since the former has capacity for roughly zero process residues.

The use of various catalysts in thermo-chemical conversion processes can be employed to enhance the production of biomass based chemicals [3]. In this respect, many zeolites catalysts have been adopted to either upgrade pyrolysis liquid products or to modify products' formation pathways so as to improve the yield of desirable products [5–8]. Bio oil of lower oxygenated components was reported by Lappas et al. [9] using FCC and commercial ZSM-5 catalysts. Amounts of water, coke and gases were found to be higher compared to pyrolysis without catalyst. Adam et al. [5] reported improved yield in furans and acetic acid over four mesoporous Al-MCM-41 catalysts. The result showed reduction in the predominance of syringyl and guaiacyl, phenolic compounds characterised of lignocellulose-derived bio oil. Similarly, levoglucosan, one of the main pyrolysis products of cellulose was completely eliminated. The authors attributed this effect to the nature and pore sizes of the catalyst. Similar reports on volatile products' fractions and reduction or total elimination of levoglucosan have been published by other authors using various modified zeolites catalyst [10,11].

Gayubo et al. [7] have demonstrated the convertibility of oxygenated pyrolysis volatile products into hydrocarbons. This was

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doi:10.1016/j.jaap.2011.03.007

achieved by the passage of vapours of model feedstock over ZSM-5 catalyst, similar to the method of Horne and William [12]. In a related work, theoretical aromatics yield of between 35 and 50% has been reported from the pyrolysis of wood and cellulose feedstock with ZSM-5 catalyst in a fixed bed micro reactor [13]. It was also noted that the product selectivity was chiefly determined by reaction conditions and the nature of active sites in the catalyst. The aromatics yield was significantly improved by high catalyst to feed ratio [14].

The role of the zeolites active site on the nature of the volatile products obtained in biomass pyrolysis has similarly been investigated by other authors [15,16]. The result of catalytic pyrolysis of softwood in continuous fluidized bed carried out by Aho et al. [17] indicated that β-zeolite, mordernite, Y-zeolite and ZSM-5 catalysts generated different products pattern. Reductions in the amounts of acetic acid and alcohols were noted. Unlike the chemical composition of the bio oil, the yield of the products was less influenced by catalyst properties.

Attempts to obtain high yields of individual pyrolytic volatile products have been made by various authors [15,18–20]. An improvement in the yield of levoglucosan and levoglucosenone was reported by Fabbri et al. [18] when cellulose was pyrolysed with nanopowder of five metal oxides (SiO_2, Al_2O_3, MgO, $TiSiO_4$ and $Al_2O_3TiO_2$). In contrast, three zeolite catalysts (H-Y, NH4-Y, NH4-ZSM-5) tested alongside with the nanoparticles generally induced reduction in the amount of anhydrosugars. A closely related conclusion on the yield of levoglucosan and other anhydrosugar was reached by Torri et al. [15], who employed six mesoporous catalyst of the form MCM-14 doped with Al, Mg, Ti, Sn or Zr for offline pyrolysis of microgranular cellulose. They however reported a high yield of 3-hydroxy-5-hydroxymethyltetrahydrofuran-3-carboxylic acid. Improvement in the yield of levoglucosan from biomass has mostly been achieved as reported by previous authors following modification or pre-treatment of feeds. Dobele et al. [19] observed that the use of phosphoric acid for the pre-treatment of biomass and cellulose prior to pyrolysis significantly affect levoglucosan yield. Depending on the acid concentration, up to 27.3% and 44.8% yield of the anhydrosugar were obtained from both feeds respectively.

Most previous work in the area of catalytic conversion of biomass using zeolite catalysts have either been devoted to the upgrade of the liquid product or the production of hydrocarbon from biomass with improved fuel properties [21–23]. This has been mostly achieved by allowing the volatile products to diffuse through the zeolites layer. However, there is scanty information on the effect of the zeolites on emerging products when directly mixed with the biomass during the conversion process. The focus of this work therefore is to the study the effect of different zeolites on lignocellulose pyrolysis products in a system where both feed and catalysts are directly mixed in a manner similar to FCC unit operation.

2. Materials and methods

2.1. Catalyst

To study the influence of pulverized zeolites on biomass volatile products, five zeolites employed in the analytical pyrolysis experiments were SN-27, MSN-15, MSM-15, H-ZSM-5-80 and H-ZSM-5-28. Both SN-27 and MSN-15 are sodium form while MSM-15 and H-ZSM-5 are ammonium and hydrogen forms respectively. The conversion of the MSM-15 to hydrogen form was effected through calcination in a furnace at 400 °C for 5 h while other catalysts were also reactivated in the furnace. All catalysts employed have dual channel systems. Basic properties of the catalysts are summarised in Table 1.

2.2. Biomass

Beech (*Fagus sylvatica* L.) wood, obtained from J. Rettenmaier & Söhne GmbH, Rosenberg, Germany was used as feedstock. The physico-chemical analysis of the materials has been carried out by Azeez et al. [24]. To obtain uniform mixture of feed and catalyst, the lignocellulosic materials was milled with various catalysts using a SPEX 6750 Freezer Mill to obtain <100 μm particle size.

2.3. Pyrolysis-GC/MS/FID

Between 80 μg and 140 μg of biomass thoroughly mixed with varying amount of catalysts was weighed into stainless pyrolysis cup. With the aid of Py-2020iD micro-furnace pyrolyzer (Frontier Laboratories Ltd.) mounted on an Agilent 6890 GC system, the thermo-chemical conversion was carried out in preheated furnace within 12 s at 500 °C and the pyrolysis vapour flushed with helium gas into the GC column. The GC was fitted with a VF-1701 (Varian) fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thicknesses), Flame ionization detector and an Agilent 5973 mass selective detector (electron ionization at 70 eV, ion source temperature at 280 °C). For effective separation of the components, the oven temperature was held at 45 °C (4 min) and raised to 255 °C at 3 °C min^{-1} (70 min) using He as carrier gas (1 ml min^{-1}). A duplicate measurement was carried out for each analysis.

2.4. Data treatment

The chromatographic peaks on the MS signal obtained from total ion chromatogram (scan mode) were identified using Mass Finder 4 by comparing their mass spectra in NIST and home-developed libraries. MS signals were used for the purpose of identification and the peak areas in FID signal were used for quantifications. Peak areas were normalised by sample weight and average values of duplicate runs were obtained. Unscrambler 8.0 was used for the Principal Component Analysis (PCA) of the pyrolysis products.

3. Results and discussion

3.1. Effects of catalyst type

About 85 volatile components similar to those found in our previous work [24] were identified in chromatograms of treated and untreated samples. To study the effect of various zeolites on major volatile products from beech wood, peak areas from FID signal of identified components in sample doped with catalyst were divided through corresponding peaks in untreated sample (US). The result of the ratios is depicted in Table 2. Meanwhile, quantified weight percentage of these pyrolysis components from the same sample (beech) and its yield have been reported in our previous work [24].

The result indicates that the catalysts have specific effects mostly on volatile components derived from cellulose and hemicellulose. Even in cases of yields' reduction in some low molecular products, the extent of the reduction varies notwithstanding as noted in ratios of acetol, 3-butenal-one, 3-pentanone and 2-hydroxy-3-methyl cyclopentene-1one.

Samples treated with catalysts yield lower holocellulose derived products such as hydroxy acetaldehyde, acetic acid and hydroxy-propanone. These products are often noted with prominent peaks in chromatograms (Py-GC/MS) of lignocelluloses. The extent of the reduction is minimal and negligible in some instances. The specificity of the zeolites is less pronounced among lignin derived products such as guaiacol, 4-vinyl guaiacol, syringol and 4-vinyl syringol. Exceptional cases to this observation are probably occasioned by secondary fragmentation of these products such as sinapaldehyde into 4-methyl syringol. The secondary product can

Table 1
Properties of catalysts.

Catalyst	Source	Composition		Pore opening size (nm)		Crystal structure
		SiO_2/Al_2O_3 molar ratio	Na_2O	Straight channels	Sinusoidal channels	
SN 27	ALSI-PENTA Zeolithe GmbH, Germany	24–27	<4%	0.53 × 0.56	0.51 × 0.55	Pentasil (MFI)
MSN-15	ALSI-PENTA Zeolithe GmbH, Germany	13–15	<4%	0.65 × 0.70	0.26 × 0.57	Mordenite
MSM-15	ALSI-PENTA Zeolithe GmbH, Germany	13–15	<0.07%	0.65 × 0.70	0.26 × 0.57	Mordenite
H-ZSM-5-80	Degussa AG, Germany	80	<0.05%	0.53 × 0.56	0.51 × 0.56	Pentasil (M FI)
H-ZSM-5-28	Degussa AG, Germany	28	<0.05%	0.53 × 0.56	0.51 × 0.56	Pentasil (MFI)

subsequently react with low molecular products from holocellulose to form indene compounds.

The PCA result for untreated and catalysed samples is depicted in Fig. 1. It illustrates effects of the zeolites based on their activities. Approximately 75% of the validated variations in all the tested samples are described by PCs 1 and 2. Again, the categorisation in both PCs is majorly influenced by carbohydrate derived volatile products. The discrimination of MSM-15, HZSM-5-28 and HZSM-5-80 from other two catalysts by PC1 explains about 50% of the variation occasioned by acidic property of the catalysts. This observation arises from improved yield of components such as 3-furaldehyde **(22)**, 3-hydroxy-5,6-dihydro-(4H)-pyran-4-one **(39)**, 4-methyl-syringol **(65)**, 6, hydroxyl-5, 7-dimethoxy-1H-indene (**75**), 6-hydroxy-7-methoxy-1H-indene **(68)**, and 1,6-anhydro-β-D-glucopyranose **(76)** and anhydrosugar (**51**) among others. The delineation of the second PC is influenced by Si/Al which enhance the production of chemical products such as 2-cyclopentene-1-,4-dione (**29**), 2,3-butandione (**3**), 2-furaldehyde **(26)**, and indenes **(68, 69 and75)**.

Both SN-27 and MSN-15 zeolites with sodium active site have the least significant effect on the beech sample (as delineated by PC2) aside their enhancement of 2-butenal yield. The alkali metal act to suppress the production of volatile products whose formation is via aldol-condensation reaction as seen in the ratio of anhydrosugars formed (Table 2). The monovalent ion inhibit the formation of levoglucosan and other anhydrosugars [25,26]. Wang et al. [27] noted that this phenomenon results from the lowering of the pyrolysis temperature of lignocellulosic biomass by basic catalysts. This observation is suggestive of the fact that the mitigation is occasioned by less energetic fragmentation of sugar moiety at the temperature lower than required, for effective transglycosylation process to occur. Choudhary and Srinivasan [28] noted that the presence of sodium ion can hindered the diffusivity of high molecule (anhydrosugar for example) due to reduction in the effective channel diameter. A closely related conclusion on the reduction of catalyst activity in sodium doped zeolite have also been drawn by other authors [29].

Table 2
Peak area ratios of selected pyrolysis volatile products.

Assigned no	R.T.	Components	Weight normalised peak area ratio[a]				
			SN27	MSN-15	MSM-15	HZSM-5-28	HZSM-5-80
3	5.95	Butandione, 2,3- (diacetyl)	1.4	1.1	0.9	1.1	1.7
4	6.40	3-Pentanone	0.7	0.8	0.3	0.5	0.9
5	7.11	Acetaldehyde, hydroxy-	0.8	1.0	0.6	0.8	0.6
6	7.92	Butenal-2; crotonaldehyde trans	1.6	1.3	0.9	1.0	1.0
7	8.18	Acetic acid	0.9	0.9	0.9	0.8	0.9
10	9.67	Acetol (hydroxypropanone)	0.7	0.7	0.3	0.4	0.5
17	14.41	Propionaldehyde, 3-hydroxy	1.0	1.0	0.9	0.9	0.9
19	14.95	Furanone, 2(3H)-	0.9	1.1	0.7	0.7	0.6
20	15.05	Butenal-2-one, 3-	0.8	0.8	0.2	0.3	0.2
22	15.98	Furaldehyde, 3-	1.4	1.3	1.6	1.6	2.4
26	17.38	Furaldehyde, 2-	1.8	1.2	1.6	1.5	4.2
29	21.87	2-Cyclopentene-1,4-dione	1.5	1.2	1.2	1.3	2.5
31	23.03	Cyclopentene-1-one, 2-hydroxy-2-	0.7	0.8	0.5	0.6	0.6
32	24.05	Furan-x-one, x,x-dihydro-x-methyl-	1.0	1.2	1.1	1.0	0.5
35	25.97	Furanone, 2(5H)-	1.0	1.2	0.7	0.8	0.7
39	27.04	Pyran-4-one, 3-hydroxy-5,6-dihydro-(4H)-	1.6	1.5	2.1	2.0	1.4
40	27.91	Cyclopenten-1-one, 2-hydroxy-3-methyl-2-	0.5	0.6	0.3	0.4	0.3
41	28.15	Pyran-2-one, 3,4-Dihydro-6-methyl-2H-	1.7	1.5	2.1	2.4	1.4
43	30.44	Guaiacol	0.9	0.9	1.1	1.1	1.0
51	39.38	Anhydrous unknown sugar	2.0	2.2	3.9	3.7	3.1
56	41.69	Guaiacol, 4-vinyl-	0.9	0.9	0.8	0.9	0.9
59	43.94	Syringol	0.9	0.8	0.8	1.0	0.8
61	45.03	Furanone, dihydro-4-hydroxy-2(3H)-	0.9	0.9	0.6	0.7	0.5
63	47.30	Guaiacol, 4-propenyl-; (isoeugenol) trans	1.1	1.2	0.7	0.8	1.2
64	47.50	Anhydro-β-D-xylofuranose, 1,5-	1.0	1.0	8.3	8.3	2.1
65	47.66	Syringol, 4-methyl	1.1	1.2	1.5	1.4	1.3
68	48.72	Indene, 6-Hydroxy-7-methoxy-1H-	1.1	0.9	1.3	1.1	1.9
69	49.12	Indene, 6-hydroxy-7-methoxy-, 2H-	1.0	0.9	1.1	1.1	1.5
72	52.87	Syringol, 4-vinyl	0.9	0.9	0.8	0.8	0.9
73	53.49	Syringol, 4-allyl-	1.0	1.1	1.1	1.2	1.0
75	56.83	Indene, 6-hydroxy-5,7-dimethoxy-1H-	1.1	1.1	1.8	1.6	2.7
76	57.17	Anhydro-β-D-glucopyranose (levoglucosan)	1.9	2.1	7.9	6.7	5.7
77	57.76	Syringol, 4-(1-propenyl)- trans	1.0	1.1	1.2	1.2	1.0
78	58.74	Syringaldehyde	1.1	1.1	1.0	1.1	1.0
81	61.07	Acetosyringone	1.1	1.0	0.8	0.9	0.9

[a] Weight normalised peak area ratio = weight normalised peak area treated sample/weight normalised peak area untreated sample.

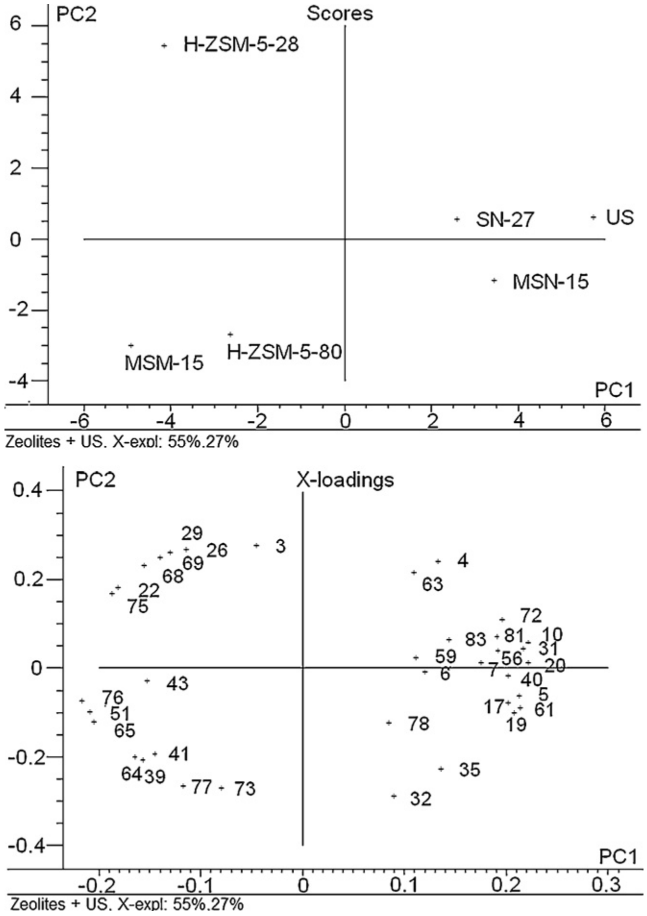

Fig. 1. Score and x-loading plots of PC1 vs. PC2 for major volatile products.

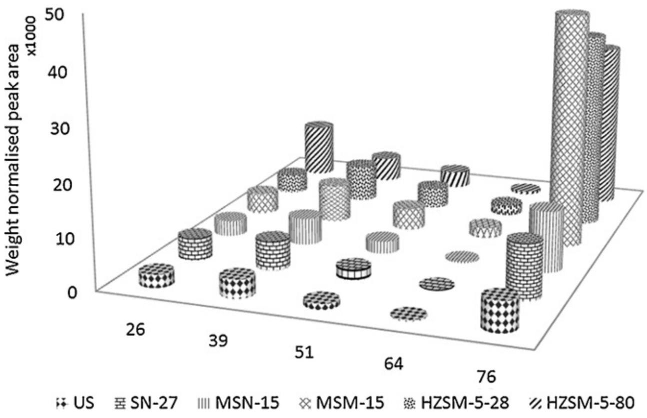

Fig. 2. Distributions of some volatile products from beech holocellulose.

The result of major effects of zeolites on some holocellulose derived products in samples treated with 30% zeolites and untreated sample (US) is depicted in Fig. 2. An increase in the concentration of products; 2-furaldehyde (26), 3-hydroxy-5, 6-dihydro-(4H)-pyran-4-one (39), anhydro xylofuranose (64) and levoglucosan (76), is noted across almost all catalyst, although with varying degree. These compounds are cyclic-products directly obtained from pentose and hexose sugars via transglycosylation, dehydration and cyclization reaction processes. In contrast, concentrations of fragmentation products such as acetic acid, hydroxyacetaldehyde, 3-pentanone, 2(3H)-furanone and 3- butenal-2-one dipped (in most cases) by the action of all zeolite (Table 2). From this, it appears zeolites kinetically favour the intra-molecular ring-closing reaction of the holocellulose. Both SN-27 and MSN-15 least enhanced the concentration of products (in Fig. 2) but also with different products' selectivity. Between both sodium active zeolites, SN-27 appears to have improved the production of furfural while MSN-15 seems to have better selectivity for anhydrosugars.

The most significant influence on the volatile products yield shown in Fig. 2 and Table 2 is induced by the acidic catalysts. Dominant organic products in this regard with marked effects are 1, 6-anhydro-β-D-glucopyranose (Levoglucosan), 1, 5- anhydro-β-D-xylofuranose, furfural and an unknown carbohydrate. These products especially levoglucosan and furfural are important chemicals with wide industrial applications. All acidic catalysts preferably promote the formation of levoglucosan but with greatest enhancement by MSM-15 and HZSM-5-28 which translate to about 8 times increment in samples dosed with 30% catalysts compared to the untreated sample. Initial percentage peak areas of furfural and levoglucosan increased from 1.4% and 3.3% in untreated sample to 4.6% and 20% in sample treated with HZSM-5-80 and MSM-15 in which they respectively have highest yields (Fig. 3a and b). While increased yield of furfural upon the application of zeolite catalyst to lignocelluloses have also been observed by Adam et al. [5], the observation on the yield of levoglucosan is exceptional if juxtaposed with reports by previous authors [5,10,18]. The discrepancy could be related to the selectivity of different catalyst employed by the authors or the method of sample preparation.

Small pores of zeolite catalysts with varying characteristics accommodate active sites and often determine selectivity in reactions. Csicsery [30] explained that the selectivity arise from three forms namely reactant shape selectivity, product shape selectivity and transition state selectivity. However, transformation of molecules by zeolites occurs not exclusive by diffusion. There exist externally active sites on zeolites' surface area and their pore mouth region. Chemical reactions on zeolites surface area limits reactivity through diffusion processes as a result of pore blockage [31]. Therefore transformation of molecule by zeolites is not exclusive through diffusion.

The tested zeolites exhibit selectivity in their enhancement of various decomposition products. This variation is even noted in both H-ZSM-5 zeolites. Both H-ZSM-5 favour the production of high anhydrosugars but with slightly higher yield in H-ZSM-5-28. On the other hand, H-ZSM-5-80 selectively enhanced high yields of furfural as shown in Fig. 3b. The only difference between both catalyst lies in the silica-alumina ratio, which resulted in (both having) different acidic strengths. The introduction of alumina into zeolites usually increases electronegativity, which is compensated by hydrogen in zeolite. Therefore, H-ZSM-5-28 with lower SiO_2/Al_2O_3 is more acidic than H-ZSM-5-80. Consequentially, the marked effect of the MSM-15 with respect to the highest amount of levoglucosan produced is related to its alumina content.

Silica-to-alumina ratio has been noted to enhance the role of Brönsted acidity in the activity of zeolite catalysts [32]. Beside the strength of active sites, their location on zeolites catalyst is another factor that can influence their functionality. It has been observed that extra framework alumina (EFAL) promotes inductive effects with respect to Lewis acid sites present around the Brønsted acid sites. These two sites are the active sites that determine the reactivity of zeolites [33]. While the former is related to the EFAL, the latter is connected to aluminium located in the framework of zeolites.

On the sample preparation, it was observed in pre-trials of the various catalysts used without prior activation in furnace that the activities of various catalysts were negligible on the amount of levoglucosan and some other volatile products obtained. This phenomenon could have arisen due to the absorption of moisture on

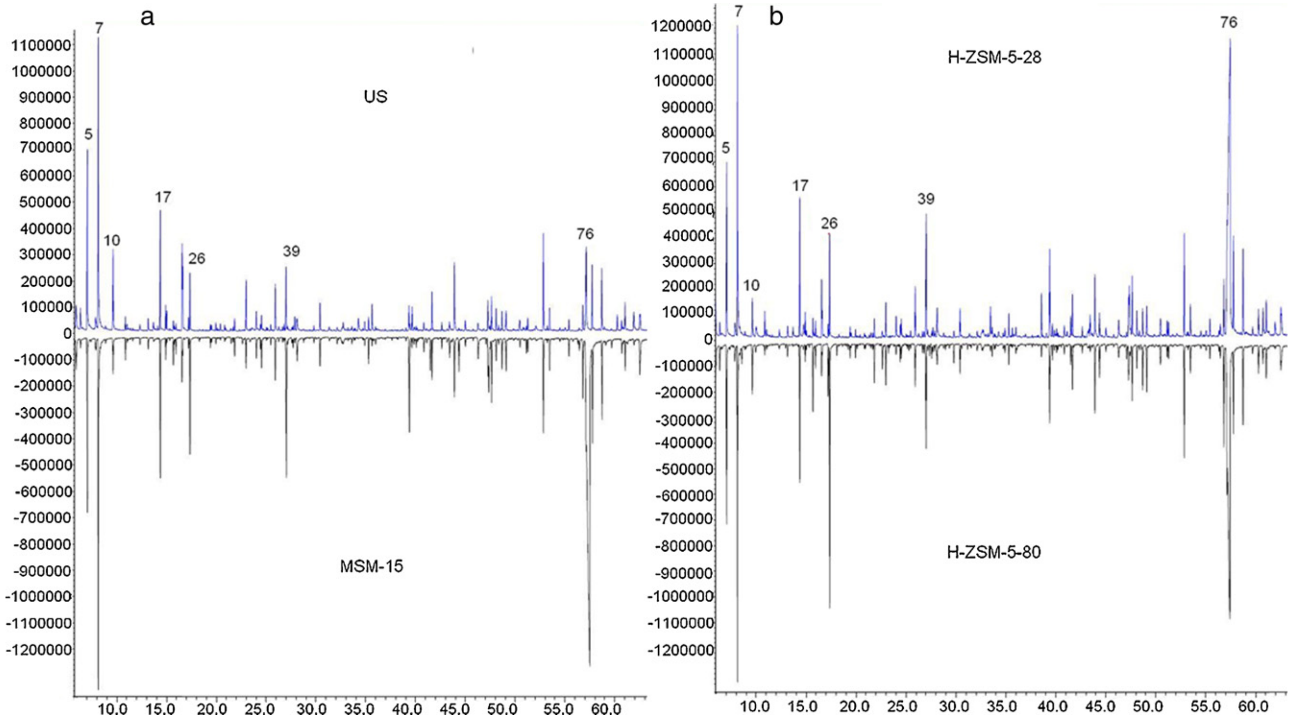

Fig. 3. TIC signals of (a) OS against MSM-15 catalysed sample and (b) H-ZSM-5-28 vs. H-ZSM-5-80 catalysed sample.

active sites of catalysts, thereby reducing the activity of the catalyst. The chromatogram of the sample with inactivated zeolite is identical with that of the untreated sample. In addition, the biomass sample was thoroughly mixed with the catalyst to form homogenous powder. There was a close interaction between the volatile product and surface area of the catalysts. This in effect is expected to produce a different result when compared to a condition in which the catalyst was introduced as a thin bed above the sample as carried out by Pattiya et al. [16].

The role of acidity in the promotion of anhydrosugar formation during fast pyrolysis has been widely investigated [34,35]. Dobele et al. [34] have opined that the cellulose glycosidic bonds undergo easy cleavage under the hydrolytic action of acid. And since depolymerisation step preludes the formation of levoglucosan via

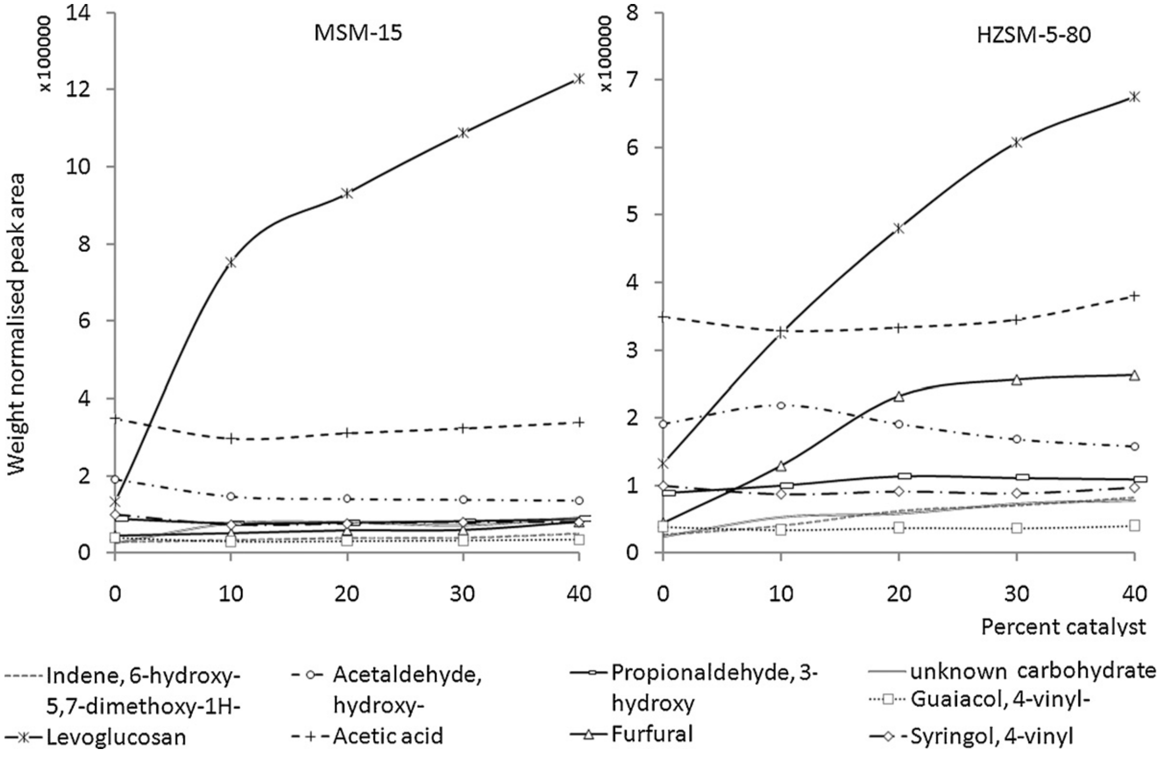

Fig. 4. Influence of catalyst concentration on most prominent volatile products.

transglycosylation, it could be deduced that the acidic zeolites act just like mineral acid by protonating the glycosidic oxygen. This results in the production of monomers of cellulose unit through which high yield of anhydrosugars is obtained. The suggested phenomenon can arise from transfer of proton from the Bronsted acid sites located outside zeolites pores as suggested by Zheng et al. [36].

In addition, it observed from SEM images of untreated sample and sample treated with 40% MSM-15 that chars formed after pyrolysis are much significantly smaller in the later. This morphological change is observable as a result of effective depolymerisation of the cellulose units. Although the yield of levoglucosan triply increased when impregnated with 1% phosphoric acid as reported by Dobele et al. [34], results obtained under the action of MSM-15 and HZSM-5 acidic zeolites are outstanding.

3.2. *Effect of catalyst concentration*

In order to evaluate the role of zeolites concentration on the yield of major pyrolysis products, samples with gradient concentrations between 10% and 40% of MSM-15 and HZSM-5-80 on the basis of the biomass weight were prepared and duplicate pyrolysis were carried out for each sample. Yields of levoglucosan, furfural and some low volatiles responsible for the discrimination projected by PC2 were evaluated. According to the result obtained as shown in Fig. 4, only levoglucosan yield was substantially influenced by different concentration in samples containing MSM-15 while furfural yield in addition to the anhydrosugar was greatly altered in HZSM-5-80 with moderate increase in the amount of 6-hydroxy-5,7-dimethoxy-1H-indene. These observations further validate previous results (discussed above) on the influence of the zeolites catalysts on lignocellulosic biomass. The result concurs with the findings of Carlson et al. [14] that low feed-to-catalyst ratio improves products yield. It further buttress previous assertion on the limited role of molecular diffusion through zeolites' pore in the when the reactivity of the zeolite particles' surface area is high [31].

4. Conclusions

The use of various catalysts to enhanced high yield of important chemical volatile products from lignocellulosic biomass is an option that could help to positively turn around the fortune of chemical industries that basically depend on petroleum as their raw materials. Zeolite is a catalyst of choice to attain this goal because they are regenerable. Based on results obtained in this work, their action on the volatile products composition appeared to be highly selective depending on the method of sample preparation and the nature of the zeolites active sites. The acidic zeolites proved most influential on biomass pyrolysis volatile products.

High yield of levoglucosan obtained from the acidic zeolites were possibly resulted from the predominance of dehydration process following the depolymerisation by the acidic zeolites. The amount of furfural is significantly enhanced by the catalyst with the highest silica-to-alumina ratio due to less activity at the surface area of the zeolite. There is also probable contribution of diffusion process in the production of this pyrolysis product. Just like Choudhary and Srinivasa have opined that increase Si/Al boost zeolite pores. It has also been found out that ease of diffusion accounts for higher yield of furfural obtained in modernite zeolites compared to faujasites [37]. The method of sample preparation, which ensured close interaction between the catalyst and the sample mighty also have played a major role in the observed phenomenon.

Fast pyrolysis of the lignocellulose in a suitable reactor such as fluidised bed reactor would be necessary in order to quantitatively evaluate yields of the anhydrosugars and furfural. The use of different biomasses with varying holocellulose content will help to explain the effects of the catalysts on different major components of biomass. For example, the use of feedstock such as corn cob with high content of pentose may rapidly enhance the furfural yield when treated zeolites.

Acknowledgments

The authors appreciate the financial assistance rendered by Deutscher Akademischer Austauschdienst (DAAD), Germany for awarding PhD scholarship to Mr. Azeez. We equally thank the workers in the wood chemistry technology unit of the Johann Heinrich von Thünen-Institut, (vTi), Hamburg for their assistance in the course of the research.

References

[1] J.-P. Lange, Lignocellulose conversion: an introduction to chemistry, process and economics, Biofuels Bioproducts Biorefining 1 (2007) 39–48.

[2] A. Corma, G.W. Huber, L. Sauvanauda, P. O'Connor, Biomass to chemicals: catalytic conversion of glycerol/water mixtures into acrolein reaction network, J. Catal. 257 (2008) 163–171.

[3] A.V. Bridgwater, Production of high grade fuels and chemicals from catalytic pyrolysis of biomass, Catal. Today 29 (1996) 285–295.

[4] F. Cherubini, The biorefinery concept: using biomass instead of oil for producing energy and chemicals, Energy Convers. Manage. 51 (2010) 1412–1421.

[5] J. Adam, M. Blazso, E. Meszaros, M. Stocker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Gronli, G. Oye, Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts, Fuel 84 (2005) 1494–1502.

[6] C. Amen-Chen, H. Pakdel, C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: a review, Bioresour. Technol. 79 (2001) 277–299.

[7] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, J. Bilbao, Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite I. Alcohols and phenols, Ind. Eng. Chem. Res. 43 (2004) 2610–2618.

[8] J.F. Mathews, M.G. Tepylo, R.L. Eager, J.M. Pepper, Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst, Can. J. Chem. Eng. 63 (1985) 686–689.

[9] A.A. Lappas, M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, I.A. Vasalos, Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals, Fuel 81 (2002) 2087–2095.

[10] L. Qiang, L. Wen-zhi, Z. Dong, Z. Xi-feng, Analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) of sawdust with Al/SBA-15 catalysts, J. Anal. Appl. Pyrolysis 84 (2009) 131–138.

[11] A. Aho, N. Kumar, A.V. Lashkul, K. Eränen, M. Ziolek, P. Decyk, T. Salmi, B. Holmbom, M. Hupa, D.Y. Murzin, Catalytic upgrading of woody biomass derived pyrolysis vapours over iron modified zeolites in a dual-fluidized bed reactor, Fuel 89 (2010) 1992–2000.

[12] P.A. Horne, P.T. Williams, Reaction of oxygenated biomass pyrolysis model compounds over a ZSM-5 catalyst, Renewable Energy 7 (1996) 131–144.

[13] R.K. Sharma, N.N. Bakhshi, Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals, Can. J. Chem. Eng. 69 (1991) 1071–1081.

[14] T. Carlson, G. Tompsett, W. Conner, G. Huber, Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks, Top. Catal. 52 (2009) 241–252.

[15] C. Torri, I.G. Lesci, D. Fabbri, Analytical study on the pyrolytic behaviour of cellulose in the presence of MCM-41 mesoporous materials, Journal of Analytical and Applied Pyrolysis 85 (2009) 192–196.

[16] A. Pattiya, J.O. Titiloye, A.V. Bridgwater, Fast pyrolysis of cassava rhizome in the presence of catalysts, J. Anal. Appl. Pyrolysis 81 (2008) 72–79.

[17] A. Aho, N. Kumar, K. Eranen, T. Salmi, M. Hupa, D.Y. Murzin, Catalytic pyrolysis of woody biomass in a fluidized bed reactor: influence of the zeolite structure, Fuel 87 (2008) 2493–2501.

[18] D. Fabbri, C. Torri, V. Baravelli, Effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose: an analytical study, J. Anal. Appl. Pyrolysis 80 (2007) 24–29.

[19] G. Dobele, G. Rossinskaja, T. Diazbite, G. Telysheva, D. Meier, O. Faix, Application of catalysts for obtaining 1 6-anhydrosaccharides from cellulose and wood by fast pyrolysis, J. Anal. Appl. Pyrolysis 74 (2005) 401–405.

[20] M. Sasaki, K. Takahashi, Y. Haneda, H. Satoh, A. Sasaki, A. Narumi, T. Satoh, T. Kakuchi, H. Kaga, Thermochemical transformation of glucose to 1 6-anhydroglucose in high-temperature steam, Carbohydr. Res. 343 (2008) 848–854.

[21] Q. Zhang, J. Chang, T.J. Wang, Y. Xu, Upgrading bio-oil over different solid catalysts, Energy Fuels 20 (2006) 2717–2720.

[22] S.T. Srinivas, A.K. Dalai, N.N. Bakhshi, Thermal and catalytic upgrading of a biomass-derived oil in a dual reaction system, Can. J. Chem. Eng. 78 (2000) 343–354.

[23] R.K. Sharma, N.N. Bakhshi, Catalytic upgrading of fast pyrolysis oil over hzsm-5, Can. J. Chem. Eng. 71 (1993) 383–391.

[24] A.M. Azeez, D.J. Meier, r. Odermatt, T. Willner, Fast Pyrolysis of African and European lignocellulosic biomasses using Py-GC/MS and fluidized bed reactor, Energy Fuels 24 (2010) 2078–2085.

[25] M. Kleen, G. Gellerstedt, Influence of inorganic species on the formation of polysaccharide and lignin degradation products in the analytical pyrolysis of pulps, J. Anal. Appl. Pyrolysis 35 (1995) 15–41.

[26] G.N. Richards, F. Shafizadeh, Formation of “glucometasaccharinolactones” in the pyrolysis of curdlan, A (1→3)-[beta]–glucan, Carbohydr. Res. 106 (1982) 83–91.

[27] J. Wang, M.Q. Zhang, M.Q. Chen, F.F. Min, S.P. Zhang, Z.W. Ren, Y.J. Yan, Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass, Thermochim. Acta 444 (2006) 110–114.

[28] V.R. Choudhary, K.R. Srinivasan, Sorption and diffusion of benzene in H-ZSM-5: effect of Si/Al ratio degree of cation exchange and pretreatment conditions, J. Catal. 102 (1986) 328–337.

[29] A. Dyer, A.P. Singh, Effect of cation exchange on heat of sorption and catalytic activity of mordenties, Zeolites 8 (1988) 242–246.

[30] S.M. Csicsery, Shape-selective catalysis in zeolites, Zeolites 4 (1984) 202–213.

[31] S. Zheng, H.R. Heydenrych, A. Jentys, J.A. Lercher, Influence of Surface Modification on the Acid Site Distribution of HZSM-5†, J. Phys. Chem. B 106 (2002) 9552–9558.

[32] J.W. Ward, The nature of active sites on zeolites: XI. The effects of the silica-to-alumina ratio on the acidity and catalytic activity of synthetic faujasite-type zeolites, J. Catal. 17 (1970) 355–358.

[33] T.F. Narbeshuber, A. Brait, K. Seshan, J.A. Lercher, The influence of extraframework aluminum on H-FAU catalyzed cracking of light alkanes, Appl. Catal. A: Gen. 146 (1996) 119–129.

[34] G. Dobele, T. Dizhbite, G. Rossinskaja, G. Telysheva, D. Mier, S. Radtke, O. Faix, Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis - A promising method for obtaining 1,6-anhydrosaccharides in high yields, J. Anal. Appl. Pyrolysis 68–9 (2003) 197–211.

[35] F. Shafizadeh, R.H. Furneaux, T.G. Cochran, J.P. Scholl, Y. Sakai, Production of levoglucosan and glucose from pyrolysis of cellulosic materials, J. Appl. Polym. Sci. 23 (1979) 3525–3539.

[36] S. Zheng, A. Jentys, J.A. Lercher, Xylene isomerization with surface-modified HZSM-5 zeolite catalysts: an in situ IR study, J. Catal. 241 (2006) 304–311.

[37] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, Selective preparation of furfural from xylose over microporous solid acid catalysts, Ind. Crops Products 7 (1998) 95–99.